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MECHANICS OF ENAMEL ADHERENCE: XIV, (1) ROLE OF COBALT OXIDE IN METAL AND OXIDE PRECIPITATION DURING GROUND-COAT FIRING CYCLE AND (2) DETERMINATION OF TEMPERATURE AND TIME INTERVALS OF PRECIPITATION*

By R. M. King

Abstract

The role of cobalt oxide in metal precipitation is explained on the basis of the influence of cobalt oxide on the reaction $4FeO \longleftrightarrow Fe + Fe_3O_4$. The temperature intervals during the firing cycle at which precipitation takes place and the relative rates of precipitation in ground coats of varying composition have been determined by a method of electrical conductivity at high temperatures.

I. Introduction

In this series of studies, the author and his co-workers[1] have endeavored to gather evidence which would provide substantial proof for a theory of ground-coat adherence to iron. The presence of a potential bonding agent is not sufficient proof that it functions as a bonding agent, and the presence of various metals and oxides at the ground-coat iron interface, moreover, is not in itself proof that any one or all of them has any particular role. It seems timely, therefore, to summarize the pertinent facts and items of proof found in recently reported investigations.

(1) Summary of Pertinent Facts

(1) Reprecipitated iron in dendrite form has been found at the interface of a normally fired ground coat containing 1.25% of commercial Co_3O_4 and of normally fired commercial ground coats.

(2) With 2.5% or more of cobalt oxide present in the raw batch, both cobalt and iron could be detected when enamels are fired under conditions approaching equilibrium.

(3) "Ferrous oxide" and magnetic iron oxide have been identified at the enamel-iron interface when the ground coats are fired under normal conditions or *in vacuo* but not when equilibrium is approached on firing in the open air.

(4) Dendrites of molybdenum and antimony have been detected at the enamel-iron interface of ground coats containing the oxides of these metals.

(2) Dendrite and Oxide Theories

(*A*) *Items of Proof in Favor of a Dendrite Theory:* (1) Under conditions approaching equilibrium, dendrites of iron and other metals were precipitated, and good adherence was obtained in the absence of any oxide phase; (2) firing *in vacuo* produced Fe_3O_4 as the predominant crystalline phase at the interface along with a trace of "ferrous oxide," but no iron phase was identified; adherence was unusually poor; (3) ground coats containing molybdenum and antimony oxides produced dendritic metal formations and good adherence; (4) Andrews and Swift[2] found a correlation between the degree of adherence and quantity of dendrites formed; and (5) the instability of so-called "ferrous oxide" and the proved solubility of magnetic iron oxide in ground-coat enamels do not justify their consideration as bonding agents.

(*B*) *Item of Proof in Favor of an Oxide Theory:* (1) Presence of "ferrous oxide" and magnetic iron oxide at the interface of normally fired enamels offers such proof.

The importance of results obtained under approximate equilibrium conditions by Schwartzwalder and

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This paper is a joint contribution of the Engineering Experiment Station and Department of Ceramic Engineering, Ohio State University, Columbus, Ohio.

[1] For summary of references to this series, see R. M. King, "Mechanics of Enamel Adherence: XIII, Review of Theoretical Explanations for Formation of Metal Particles in Cobalt Ground Coats and Pertinent Experiments," *Jour. Amer. Ceram. Soc.*, **20** [2] 53–55 (1937).

[2] A. I. Andrews and H. R. Swift, "Iron Oxide in Enamel Glass as Dissolved from Metal Base," *Jour. Amer. Ceram. Soc.*, **25** [May 1, No. 9] 217–22 (1942).

King[3] and by Spencer-Strong and King[4] cannot be overemphasized. It is only under such conditions that stability, with respect to the phases present, can be obtained. If iron oxides were not present at equilibrium, it would seem that these oxides are so much debris when they are present in the normally fired enamels. If, however, iron is present and good adherence is obtained, this fact indirectly, at least, favors a dendritic theory of adherence.

It should be recalled that Dietzel and Meures[5] have presented a theory of adherence, based on a gradation of coefficient of expansion resulting from a solution of iron oxide in the enamel. It is not apparent, however, how a change in the coefficient of expansion would increase those bonds normal to the surface (which are the adhering bonds). It is true that differences in expansion between enamel and iron set up stresses within the glass parallel to the interface and that a graded coefficient of expansion would conceivably lessen the stresses tending to rupture the glass and break the adhering bonds, but these effects would not alter the strength of these bonds. When a ground coat ruptures under excess stress, the enamel breaks within itself and seldom leaves a clean steel surface, thus indicating that the forces normal to the steel are stronger than the cohering bonds within the glass. It seems, therefore, that favorable expansion of the glass aids adherence in a negative rather than in a positive manner.

II. Explanation of Role of Cobalt in Metal and Oxide Precipitation During Ground-Coat Firing Cycle

Despite the large number of investigations of ground-coat adherence during recent years and the discovery of some of the effects of the addition of cobalt oxide to a ground-coat enamel, little work has been done to show why its action is so unique. If iron dendrites or iron oxide are necessary for adherence, why is it necessary to add cobalt oxide to produce them and why has the enamel industry been unable to produce them by the addition of iron oxide? A few theories have been proposed,[6] but they have either not been substantiated or they have been disproved. Kautz[7] has offered evidence that cobalt oxide acts as an oxygen carrier, thus bringing oxygen into a reaction which results presumably in oxide precipitation at the interface, but this does not explain the formation of metallic dendrites, particularly iron dendrites. Evidence for a more convincing role for cobalt oxide therefore appears to be desirable.

Kautz[8] and King[1] have called attention to the formation of iron through the decomposition of "FeO" at 575°C. according to reaction (1).

$$4FeO \longleftrightarrow Fe + Fe_3O_4 \qquad (1)$$

Investigators of this system disagree as to whether the compound FeO actually exists. Some evidence favors the stoichiometric compound and some indicates a series of solid solutions of iron and oxygen; but since the decomposition products are the same, the answer to this question is not pertinent to the present studies except perhaps the apparent difference in velocity and temperature of decomposition. The so-called "ferrous oxide," however, will be referred to as "FeO."

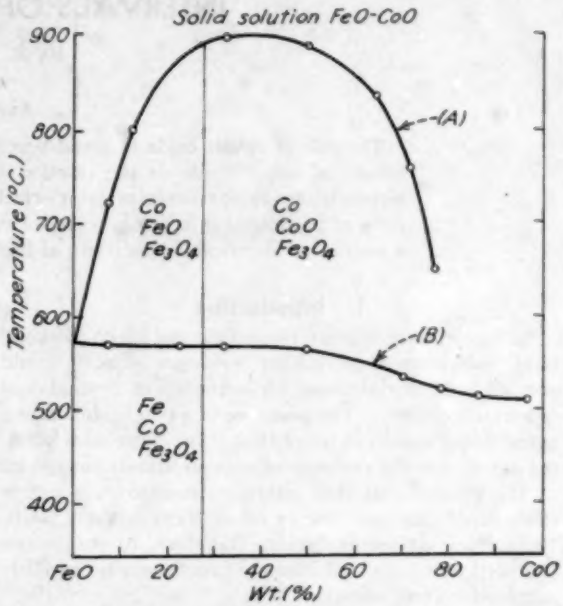

FIG. 1.—Bernard's equilibrium diagram for the solid system FeO–CoO.

Hugett[9] has studied the decomposition of "FeO" by thermomagnetic analysis, and Bernard[10] used X-ray and thermomagnetic analyses. Their findings may be summarized as follows: On heating, decomposition of a sample of "FeO," prepared by sudden quenching, began at 280°C., reached a maximum rate at about 450°C., continued up to 510°C., and decreased suddenly at 570°C., which is the equilibrium temperature of the three phases (see reaction (1)). Decomposition was complete at 620°C. On cooling, decomposition of "FeO" began at 450°C. It is apparent, therefore, that 450°C. is a critical temperature in the formation of

[3] Karl Schwartzwalder and R. M. King, "Mechanics of Enamel Adherence: VI, Petrographic, Metallographic, and X-Ray Study of Enamel-Metal Contact Zones," *Jour. Amer. Ceram. Soc.*, **15** [9] 483–86 (1932).

[4] G. H. Spencer-Strong and R. M. King, "Mechanics of Enamel Adherence: IX, Equilibrium Studies in Some Systems of Enamel Glass and Cobalt, Nickel, and Iron Oxides," *ibid.*, **17** [7] 208–14 (1934).

[5] A. Dietzel and K. Meures, "Adjustment of Enamels to Sheet Steel," *ibid.*, **18** [2] 37–38 (1935).

[6] For summary of these theories, see A. I. Andrews, Enamels, p. 166. Twin City Pub. Co., Champaign, Ill., 1935. 410 pp.; *Ceram. Abs.*, **14** [7] 158 (1935).

[7] Karl Kautz, "Observations on Function of Adherence-Promoting Oxides in Ground-Coat Enamels," *Jour. Amer. Ceram. Soc.*, **22** [8] 250–55 (1939).

[8] Karl Kautz, "Further Data on Enamel Adherence," *ibid.*, **19** [4] 93–108 (1936).

[9] J. Hugett, "Application de l'Analyse Thermomagnetique l'Étude des Oxydes et des Minerals de Fer," *Ann. chim.* [Series 10], **11** [10] 447–510 (1929).

[10] Jaques Bernard, "Étude de la Decomposition du Protoxide de Fer et de ses Solutions Solides," *ibid.*, [Series 11], **12** [1] 5–92 (1939).

iron and magnetic iron oxide from "FeO" (possibly more so than the equilibrium temperature, 570°C.).

Bernard[10] also studied the influence of cobalt, nickel, and other oxides on the decomposition reaction of "FeO" and established the equilibrium diagram shown in Fig. 1. He interpreted this diagram as follows: (1) the area of homogeneous solid solution, FeO-CoO, above curve *A*; (2) the area of magnetite and cobalt with an excess of "FeO" or CoO, depending on whether the original composition is to the left or right of the vertical line corresponding to the ratio 3FeO·CoO; and (3) the area below the horizontal line, *B*, at 570°C. with Fe_3O_4, cobalt, and iron.

In this system, therefore, the reactions are $3FeO + CoO \longleftrightarrow Fe_3O_4 + Co$ above 570°C. and $4FeO \longleftrightarrow Fe + Fe_3O_4$ below 570°C.

These established facts relating to the influence of cobalt oxide on the decomposition of iron oxide are significant in the precipitation of iron and cobalt at the ground coat-iron interface if it can be assumed or proved that cobalt oxide in the enamel glass acts similarly with the "FeO," which is formed from the iron base during firing. Such an assumption or such proof could account for the detection of iron only in fired ground coats containing 1.25% of cobalt oxide and of both iron and cobalt when the cobalt oxide content is 2.50% and higher. The equilibrium diagram indicates that the higher the ratio of CoO to FeO, up to about 35% of CoO, the higher the temperature at which metal precipitation begins and the greater the range of cobalt precipitation; therefore, the greater the range of cobalt plus iron precipitation. A greater amount cobalt, furthermore, would be expected the higher the cobalt oxide content.

Ratios of FeO to CoO in fired ground coats are not accurately known. Spencer-Strong and King[11] determined the ratio of total iron to the amount of cobalt oxide in the enamel, but they recognized some difficulty in obtaining accurate results. From these results, however, the following ratios have been calculated:

At 1.25% of CoO, FeO:CoO = 6.4:1.
At 2.50% of CoO, FeO:CoO = 5.8:1.

These ratios are about the same, and the detection of cobalt in enamels containing 2.50% and no cobalt in those containing 1.25% may be explained only by the greater amounts present. Cobalt probably was present in the enamels containing 1.25%, but it was not detected by the X-ray tests, which are not sensitive to quantities of less than 5%.

III. Determination of Temperature and Time Intervals and Metal Precipitation During Ground-Coat Firing

The fact that the decomposition of solid solutions of FeO and CoO and the firing of cobalt-bearing ground coats on iron produced cobalt, iron, Fe_3O_4, and sometimes "FeO" could not be dismissed as a mere coincidence. It seemed desirable, therefore, to try to determine the course of metal precipitation in relation to the firing cycle and cobalt oxide concentration. If the course of metal formation could be followed, that of magnetic oxide formation obviously would also be followed even though a large portion might be dissolved in the enamel.

Several possible methods were reviewed, and it was decided to measure the electrical resistance of the ground coat when fired between two enameling iron test pieces. The apparatus consisted essentially of two rivetlike test pieces, each fastened to a rod of heat-resisting alloy placed vertically so that a preheated furnace could be lowered to surround the test pieces between which a layer of the enamel was placed (see Fig. 2). Resistance was measured by means of a Wheatstone bridge.

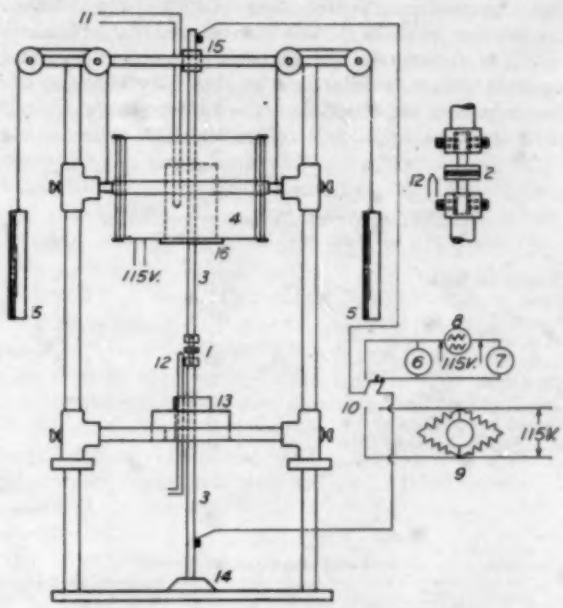

FIG. 2.—Apparatus to determine resistance of enamels: (1) Test-piece assembly; (2) detail of test-piece assembly; (3) rods of heat-resisting alloy; (4) furnace; (5) counterweights for furnace; (6) voltmeter, 1.5 volts a.c.; (7) ammeter, 3.0 amp. a.c.; (8) Variac resistance; (9) Wheatstone bridge; (10) double-pole, double-throw switch; (11) pilot thermocouple; (12) firing thermocouple; (13) block of insulating brick; (14) insulating support (rubber); (15) insulating guide (wood); and (16) asbestos cover pieces.

A resistance method was prompted by the previously established fact that metal dendrites penetrate relatively thick layers of ground coats. It was thought that a growth of dendrites would gradually bridge the gap between the two iron surfaces, and thus by following changes in resistance, the response of metal precipitation to the firing cycle and to cobalt oxide concentration could be determined.

Speculation as to this response in a ground-coat enamel obtained from information revealed by the equilibrium diagram was as follows: (1) If metal be precipitated during cooling, resistance at low temperatures should be low rather than the high resistance which is characteristic of glass at low temperatures.

[11] G. H. Spencer-Strong and R. M. King, "Mechanics of Enamel Adherence: V, Study of Enamel-Metal Contact Zones by Chemical Methods," *Jour. Amer. Ceram. Soc.*, **15** [9] 480–83 (1932).

(2) Inasmuch as metal precipitation from the solid solutions increases during cooling, resistance of ground coats should decrease as temperature decreases.

(3) If enough metal is precipitated to lower markedly the resistance of the ground coat at low temperatures, the resistance should increase at some interval of the reheating period since the reactions involved are reversible.

(4) As long as oxidation occurs and cobalt oxide is available, minimum values of resistance should decrease as firing is repeated.

(5) Enamels containing no cobalt oxide should show higher resistances than those containing this oxide and should show also increasing resistance on cooling.

After considerable preliminary work, it was found that a ground coat, fritted from 98.49% of the cobalt-free portion of the soft base enamel (see Table I) and 1.51% of commercial cobalt oxide (Co_3O_4) and given repeated firings, exhibited a gradual development of the properties expected from the interpretation given in the equilibrium diagram (Fig. 1.) The behavior of this enamel was selected for comparison with that of other enamel compositions.

TABLE I

ENAMEL GROUND-COAT COMPOSITIONS

	Soft	Hard
Potash feldspar	31.0	31.0
Flint	11.4	18.0
Borax	37.1	37.1
Soda ash	5.9	5.9
Sodium nitrate	3.8	3.8
Fluorspar	9.0	3.0
Cobalt oxide (Co_3O_4)	0.5	0.5
Nickel oxide (Ni_2O_3)	0.4	0.6
Manganese dioxide (MnO_2)	0.9	1.1

(1) Procedure

(*A*) *Firing Routine:* Initial firing to 1658°F. within 3 minutes; second, third, and fourth firings to 1658°F. within 2 minutes; and fifth firing to 1689°F. within 2.5 to 3 minutes.

(*B*) *Cooling:* Temperatures at end of (*a*) the first minute, 650°F.; (*b*) the second minute, 386°F.; (*c*) the third minute, 340°F.; and (*d*) the fourth minute, 295°F.

(*C*) *Preparation of Enamels:* Frits were smelted in a small laboratory furnace and ground to pass a 200-mesh screen; they were used dry without mill additions in all tests except when it was necessary to obtain results from a commercial enamel as usually prepared.

(*D*) *Preparation of Surface of Test Pieces:* The standard method of cleaning surfaces consisted of washing twice in carbon tetrachloride and wiping with a clean dry cloth; for some tests, the surfaces were pickled. These are shown in Table II.

(*E*) *Preparation of Test Film:* When powdered frit was used, the dry powder was placed on the face of the lower test piece (after it was cleaned with carbon tetrachloride) and fastened in a level position; an insulating spacer about 0.015 in. thick was placed on top, and the upper test piece was brought into uniform contact. When enamels were fired before the circuit was completed, they were applied in paste form.

(*F*) *Heating of Furnace:* The furnace was brought to a predetermined temperature, sufficient to reach

TABLE II

RESISTANCE DATA

Enamel No.	Ground-coat test piece description*	Firing cycle No. 1†					Firing cycle No. 2†				
		H1	H3	C1	C2	C3	H1	H2	C1	C2	C3
	Enamels fired under standard conditions										
	Temp. (°F.)	1590	1658	650	386	340	1590	1658	650	386	340
		Resistance (ohms)									
S-0-1	Soft base, 0% cobalt oxide	1.7	1.0	50	5×10^3	9×10^4	1.5	1.02	150	6×10^3	12×10^4
S-1-1	Soft base, 0.79% cobalt oxide	1.5	0.54	30	200	180	3.3	0.58	16	18	14
S-2-1	Soft base, 1.51% cobalt oxide	1.2	0.68	20	20	17	1.2	0.78	1.53	1.16	0.99
S-2-1 (calc.)	Calcd. from *S*-0-1 and *S*-2-1	4.08	2.08	33.3	20.1	17	6.0	3.23	1.55	1.16	0.99
S-3-1	Soft base, 3.05% cobalt oxide	1.4	0.44	0.45	0.38	0.35	0.50	0.37	0.29	0.28	0.28
S-4-1	Soft-ground complete	1.4	0.95	6.5	7.0	6.2	1.0	0.94	3.3	2.75	2.41
S-0-2	*S*-0-1 on 1/2-in. platinum		6.2	50	2500	46×10^3		6.2	48	3700	5×10^4
S-3-2	*S*-3-1 on 1/2-in. platinum		5.6	100	3×10^3	3×10^4		6.9	90	3×10^3	38×10^3
	Enamels fired under conditions indicated										
	Temp. (°F.)	1590	1658	650	386	340	1590	1658	650	386	340
		Resistance (ohms)									
S-H-1	40% soft and 60% hard ground-coat frits	1.44	1.04	23.5	4×10^3	75×10^3	10	1.18	30	80	71
C-1-1	Commercial blend frits only	1.52	0.59	27	10^3	12×10^3	1.50	0.72	19	970	15×10^3
C-2-1	Complete commercial 1/4-in. pickled (0.015 in.-spacer)	1.17	0.61	20	900	10^4		0.67	20	900	15×10^3
C-2-2	Complete commercial 1/4-in. unpickled (0.010 in.-spacer)	1.56	0.81	23	1070	16×10^3		0.83	15	1090	14×10^3
	Enamels fired without spacer and before joining test pieces (film thickness, 0.0045 in.)										
	Temp. (°F.)	1568	1599	650	386	340	1590	1613	650	386	340
		Resistance (ohms)									
C-2-3	Complete commercial 1/4-in. unpickled			66	1470	18×10^3		0.225	0.175	0.169	0.169
S-0-3	*S*-0-1 on 1/2-in. platinum			64	400	1200		2.7	40	250	600
S-0-4	*S*-0-1 on 1/2-in. unpickled iron			5.0	19	33	1.54	0.69	6.0	29	85
S-0-5	*S*-0-1 on 1/4-in. unpickled iron			5.0		3×10^3		0.37	1.92	9.0	13.4
S-5-1	Soft base 10% Fe_3O_4 on 1/2-in. platinum			1.42	6800	6×10^4		1.72	20	130	500

* Base is cobalt-free portion of enamel.

† H, firing cycle; C, cooling cycle: numbers indicate approximate time in minutes.

the desired finishing temperature within the specified time. This temperature was determined by the pilot couple. The furnace was lowered over the test piece, and resistance readings were taken as indicated in section (*G*). When the firing was complete, the furnace was raised, and the bottom was covered with two pieces of $\frac{1}{4}$-in. asbestos board. Resistance readings were taken during heating and cooling.

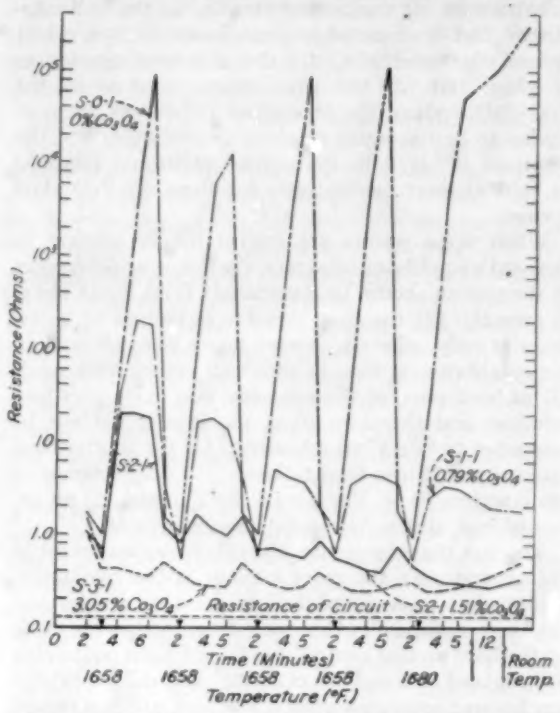

FIG. 3.—Resistance of soft ground coats containing Co_3O_4; 0%, *S*-0-1; 0.79%, *S*-1-1; 1.51%, *S*-2-1; and 3.05% of Co_3O_4, *S*-3-1; film thickness, 0.015 in.

(*G*) *Resistance Readings:* By means of the double-throw switch (10) (see Fig. 2), a voltmeter-ammeter panel or a Wheatstone bridge was connected in series with the test pieces. During heating, the volt-ammeter circuit was thrown in with the voltmeter set at 1.0 volt. Voltage and amperage were recorded when the ammeter reading was 0.50, which was usually reached at the end of 2 minutes during the first firing and at the end of 1 minute during succeeding firings. The temperature was usually about 1590°F. as read by the "firing couple." When the firing temperature was reached, readings were taken on the voltmeter and ammeter and then quickly on the Wheatstone bridge. Readings were obtained (*a*) during cooling and (*b*) at the end of each minute for 4 minutes, except during the last cooling period when readings were also recorded at the end of 10 minutes and when the test pieces had reached room temperature. Readings, when possible, were obtained from both the voltmeter circuit panel and the bridge; the latter readings were the more accurate, and they have been used in the data presented.

IV. Data

Data representative of the findings of this investigation are given in Table II and are graphically represented in Figs. 3, 4, 5, and 6. These graphs are semilogarithmic, and the curves follow resistances obtained during five firing cycles. Values for the fourth minute of cooling, which have no additional significance, have not been included. The resistance

TABLE II (*continued*)

Firing cycle No. 3†					Firing cycle No. 4†					Firing cycle No. 5†						Resistance after 24 hr. cooling
H1	H2	C1	C2	C3	H1	H2	C1	C2	C3	H1	H2	C1	C2	C3	C10	
Enamels fired under standard conditions																
1590	1658	650	386	340	1590	1658	650	386	340	1590	1689	650	386	340		
Resistance (ohms)																
1.7	1.03	30	4×10^3	8×10^4	1.7	1.06	50	6×10^3	10^4	1.7	0.90	30	5×10^3	5×10^4	10^4	3×10^4
3.6	0.59	5.0	4.4	3.5	2.0	0.63	3.5	4.85	4.2	3.3	0.53	2.4	3.3	3.1	2.05	1.97
1.5	0.68	0.76	0.62	0.55	0.93	0.58	0.51	0.43	0.41	0.77	0.46	0.35	0.30	0.29	0.28	0.35
12.8	1.98	0.76	0.62	0.55	2.07	1.55	0.51	0.43	0.41	1.39	0.95	0.36	0.30	0.29	0.28	0.35
0.48	0.33	0.27	0.26	0.26	0.39	0.31	0.25	0.25	0.26	0.31	0.32	0.25	0.26	0.27	0.35	0.50
3.2	0.94	2.43	2.05	1.78		0.93	2.23	1.86	1.63	2.45	0.92	1.74	1.48	1.31	1.2	1.88
	6.5	57	3700	5×10^4		2.3	67	4500	7×10^4		6.5	55	3300	5×10^4	52×10^4	10^5
	7.0	150	3400	4×10^4		7.0	90	4×10^3	4×10^4		67	76	4500	35×10^3	6×10^4	75×10^4
Enamels fired under conditions indicated																
1590	1658	650	386	340	1590	1689	650	386	340	1590	1689	650	386	340		
Resistance (ohms)																
4.0	0.69	26	28	23	3.7	1.05	13	14	11	4.5	1.06	6.0	6.0	5.0	3.1	2.3
1.40	0.70	25	12×10^3	14×10^3	1.50	0.77	16	120	130	1.50	0.59	12	38	36	19	14.6
1.44	0.70	15	800	11×10^3	1.50	0.58	15	650	4×10^3		0.48	35	42.5	42	29.5	23
	0.91	50	630	10^4		0.79	23	700	10^4		0.67	15	72	70	57	50
Enamels fired without spacer and before joining test pieces (film thickness, 0.0045 in.)																
1590	1635	650	386	340	1615	1658	650	386	340	1635	1689	650	386	340		
Resistance (ohms)																
0.218	0.175	0.157	0.153	0.158	0.21	0.172	0.153	0.153	0.163	0.215	0.177	0.154	0.154	0.159	0.185	0.232
	2.38	25.0	100	450		1.99	20	90	370		1.2	16	80	400	2.8×10^4	28×10^4
1.6	0.68	5.0	20	47	1.6	0.50	1.92	5.0	7.8	1.42	0.33	0.65	1.10	1.62	5.30	50
	0.33	0.84	5.2	10.0	1.8	0.295	0.33	0.295	0.29	0.40	0.26	0.228	0.223	0.223	0.241	0.30
1.68	1.28	20	104	400	1.6	1.14	15.0	45	400	1.56	0.50	17	75	300	38×10^3	35×10^4

of the test circuit, when it is short-circuited between the test rods with a steel "pin" of $^1/_8$-in. diameter, is indicated by a straight line at the bottom of the graphs.

(1) Discussion of Data

The first curve, *S*-0-1 (Fig. 3), which represents resistances of the soft cobalt oxide-free enamel, shows that there are great variations in resistance and that the resistance decreases as the temperature increases; and also as the temperature decreases, the resistance shows a marked increase. This is the normal action of a glass. Curve *S*-2-1, which represents resistances of the soft ground coat containing 1.51% of cobalt oxide, is used as a reference enamel, and some differences in the trend of values may be noted as follows: (1) the resistance decreases on cooling; (2) increases in resistance occur in the first few seconds of some of the reheating periods; (3) minimum and maximum resistances decrease with each firing cycle; and (4) on cooling to room temperature, the resistance increases slightly above the minimum.

A comparison of these results with those for the soft enamels containing 0.79 and 3.05% of cobalt oxide (see Fig. 3, curves *S*-1-1 and *S*-3-1, respectively) showed that similar results were obtained but of varying degree as the cobalt oxide content was varied; the greater the amount of cobalt oxide the lower were the resistances. The minimum resistances for *S*-2-1 and *S*-3-1 were almost as low as the circuit itself, as indicated at the bottom of the graph.

By treating the enamel and the precipitated metal as parallel circuits and by using the formula for the law of parallel resistances and the data for *S*-0-1 and *S*-2-1, the curve *S*-2-1 of the calculated data was obtained (see Fig. 4). This curve brings out more sharply the decreases and increases in resistance.

In view of (*a*) the present results, (*b*) the well-established fact that metal is precipitated at iron-cobalt ground-coat interfaces, (*c*) the abnormal resistances of glass, and (*d*) the equilibrium relations in the CoO–FeO system, the anomalous resistances are concluded to be the result of metal precipitation and the reactions involved in Bernard's equilibrium relations to hold at least qualitatively for the CoO–FeO glass system.

When these results are interpreted in relation to Bernard's equilibrium diagram, the following differences in the system should be considered: (1) A liquid phase is present; (2) the time variable is limited to a few minutes only, whereas several hours were allowed in the equilibrium studies in which all phases were solid; (3) at least some of the magnetic iron oxide goes into solution, and therefore all of the iron would not be converted to "FeO" on reheating; (4) the shorter time interval would also tend to lessen the completeness of the reaction, $Fe + Fe_3O_4 \rightarrow 4$"FeO"; and (5) an excess of iron, that is, the metal base, is present.

The fact that the greater the cobalt oxide content of the ground coat the more copious is the metal precipitate has been established in previous studies and has been confirmed in this one. Some tests were made on the hard ground coat (Table I), but a frit containing 94% of hard base and 6% of cobalt oxide did not exhibit any lowered resistance when it was fired under standard conditions. It may be said therefore that, under the firing conditions set up for the reference enamel, constituents other than cobalt oxide were effective in

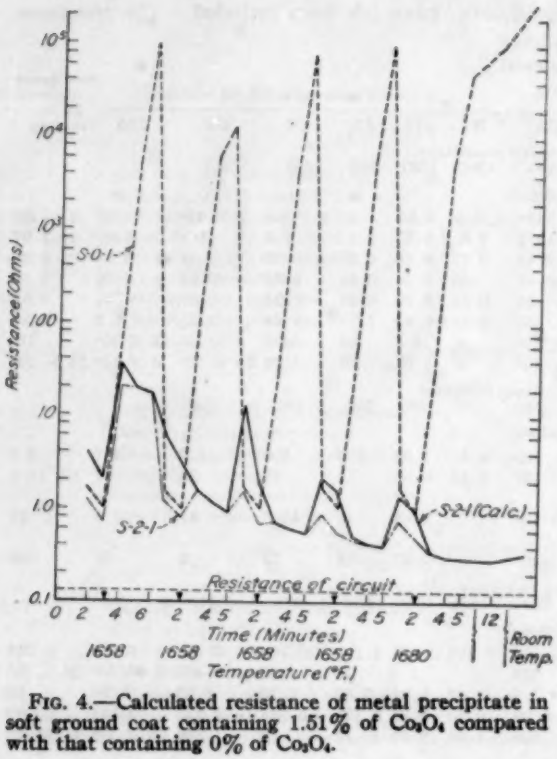

FIG. 4.—Calculated resistance of metal precipitate in soft ground coat containing 1.51% of Co_3O_4 compared with that containing 0% of Co_3O_4.

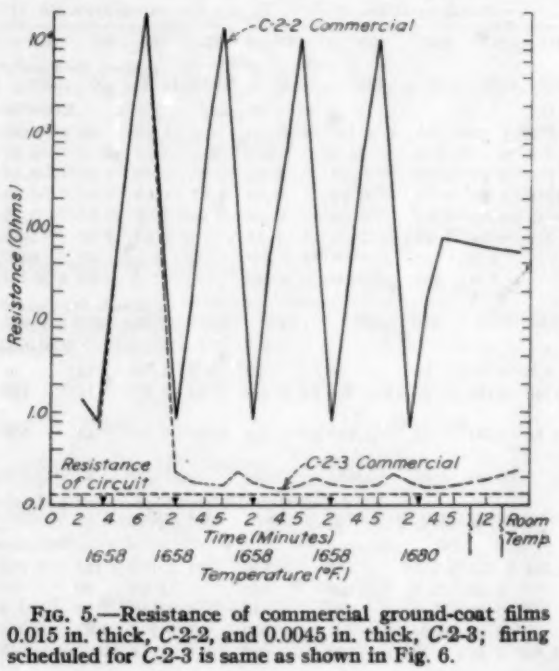

FIG. 5.—Resistance of commercial ground-coat films 0.015 in. thick, *C*-2-2, and 0.0045 in. thick, *C*-2-3; firing scheduled for *C*-2-3 is same as shown in Fig. 6.

modifying the action of ground coats. Higher firing temperatures or thinner films of enamel between the test pieces, however, would probably have shown decreases in resistance characteristic of the soft ground coats. This prediction is borne out by results from enamel *S*-H-1, a blend of the hard and soft frits of the complete ground coats, and by the results from the commercial (*C*) enamels.

The tests on the *C* group of enamels require special comment. A blend of frits of the selected commerical enamel showed no decrease in resistance on cooling until the fifth firing even though the temperature of the last two firings was 31° above the standard firing temperature. This characteristic decrease in resistance was even harder to obtain with the commerical blend prepared in the conventional manner with mill additions. Fairly consistent results were obtained, however, by increasing temperature, time of firing, and the size of the test piece and by decreasing the thickness of the enamel layer. This was especially true when no spacer was used and the enamels were fired before the test pieces were joined. In fact, results from such firings of the complete commercial enamel compare favorably with the lowest resistances obtained with any enamel even when it is fired at lower temperatures (see *C*-2-3, Table II and Fig. 5). The thickness of the enamel film in this test was about 0.0045 in. When the cobalt and nickel oxide contents were low, more time and higher temperatures apparently were required to develop metal crystals long enough to bridge the wider gaps between the test pieces and numerous enough to cause a marked decrease of resistance on cooling.

It was decided to determine whether the use of thinner layers of the soft base containing no cobalt oxide would show a decrease in resistance on cooling. The data for enamels *S*-0-4 and *S*-0-5 show a continued decrease in resistance as the number of firing cycles increased, but only slight decreases occurred on cooling (see curve *S*-0-5 in Fig. 6). It seems, therefore, that iron can be precipitated from a solution of iron oxide in a clear ground coat. That this decrease in resistance is not the result of the solution of iron oxide only is supported by the data represented by the curve *S*-5-1 (Fig. 6). This enamel contained 10% of Fe_3O_4. Resistances for this enamel were much higher even when allowance was made for the difference in the size of the test pieces. These test pieces exhibited fair adherence though not so great as that of the commercial enamels. This difference probably is a result of the relative amounts of precipitated metal.

Between the 10-minute cooling time and the time to reach room temperature, a decrease in resistance for some enamels and an increase for others may be significant. Decreases were usually observed when the cobalt content was low, which suggests the possibility that dendrites continued to grow on cooling and to make contact with the test pieces rapidly enough to bring about a net decrease in the resistance of the circuit. Minimum resistance in these enamels was usually considerably higher than those which showed an increase in resistance with the final reading.

An increase in this last reading probably resulted from the influence of the extremely high resistance (when cooled) of the enamel portion of the parallel resistances. Further study will be necessary to establish these or other explanations. It is apparent, however, at least in some enamels, that metal precipitation continues during cooling.

The foregoing discussion has emphasized chiefly metal precipitation rather than the influence of this precipitation on ground-coat adherence. It should be observed that the decomposition reactions involved produce both metal and magnetic iron oxide; the reactions therefore could affect adherence either through precipitated iron or precipitated iron oxide. Solubility of iron oxide in the enamel is unfavorable to this material as an adhering agent.

When metal precipitates can be obtained which lower the resistance of an enamel so markedly by spanning a gap of 0.015 in. and when there is no marked increase in the resistance on cooling, it seems reasonable to conclude that definite contact exists between precipitated metal and the base metal. This conclusion is another point in favor of a dendritic theory of adherence.

V. Summary and Conclusions

The most favored theories of ground-coat adherence have been reviewed, and facts supporting each theory have been listed.

A brief of Bernard's work on the influence of cobalt

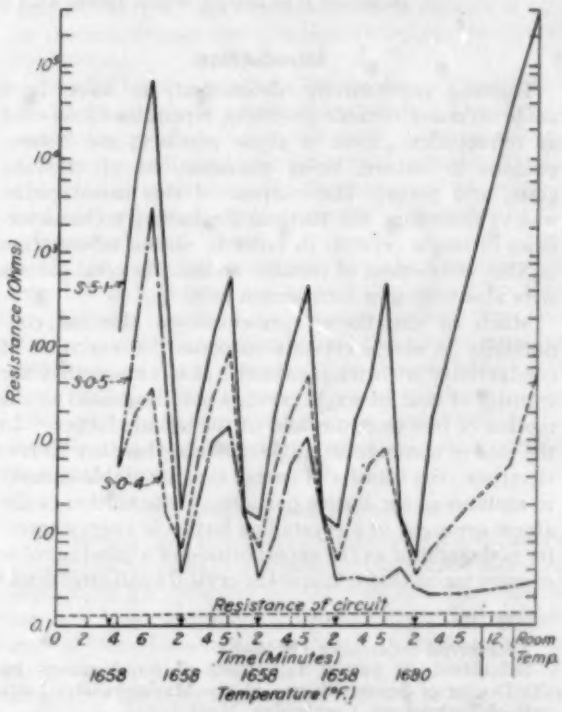

FIG. 6.—Resistance of 0% soft ground coat on 0.5-in. iron test piece, *S*-0-4; on 0.75-in. iron test piece, *S*-0-5; and of soft ground coat containing 10% of Fe_3O_4, *S*-5-1, on 0.5-in. platinum test piece; film thickness 0.0045 in.

oxide on the decomposition of "FeO" has been given, and the probable relation of his results to phases found by American investigators at ground-coat–iron interfaces have been pointed out.

A method for determining the electrical resistance of enamels during firing and cooling has also been described. By testing ground coats with and without cobalt oxide, the electrical resistance of cobalt-bearing enamels has been found to decrease with decreasing temperature and to reach a very low value on cooling. Their resistance, however, increases during a portion of the heating range. For those enamels which do not contain cobalt oxide, resistances increase on cooling and reach extremely high values. These facts have been explained by the precipitation of metal in the enamels containing cobalt oxide. This metal bridges the gap between the test pieces and causes a decrease in resistance.

It has been concluded that reactions between cobalt and iron protoxides as established by Bernard take place, at least, qualitatively at the ground coat-iron interface.

Inasmuch as magnetic iron oxide, one product of the reaction, is soluble in the enamel and since iron and cobalt, the other products of the reactions, produce such extremely low resistances, there must be intimate contact between the precipitated metal and the metal base. It was concluded that these facts favor a theory of dendritic adherence.

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THERMAL CONDUCTIVITY OF NONMETALLIC SINGLE CRYSTALS*

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Abstract

Theories of thermal conductivity in single crystals of nonmetallics are given, and the apparatus used for experimentation is described. Experimental results obtained for a number of single crystals show the variation of conductivity with temperature and crystallographic direction. A minimum thermal conductivity as the temperature is increased is indicated, which agrees with the theory of A. H. Compton.

I. Introduction

Thermal conductivity determinations have been made on many ceramic products, especially those used as refractories; most of these products are heterogeneous in nature, being combinations of crystals, glass, and pores. The purpose of this investigation was to determine the thermal conductivity characteristics of single crystals in order to obtain information on that component of ceramic bodies. Several glasses were also tested for comparison uses.

Much of the theory presented on thermal conductivity in single crystals concerns the variation of conductivity with temperature. It is known that the transfer of heat in single crystals may be traced to the motion of free electrons and of the atomic lattice. In the case of nonmetallic single crystals, there are no free electrons; the transfer of energy is attributable entirely to motions of the lattice particles. The motion of the atoms arranged in a crystalline lattice in energy transfer is thought of as the superposition of a great number of wave trains that traverse the crystal in all directions.[1] When no thermal gradient exists, no net energy is carried by the waves in any direction. Debye[2] has predicted that the thermal conductivity of a single crystal decreases rapidly with increasing temperature, and, according to Eucken,[3] the conductivity is inversely proportional to the absolute temperature. In some agreement with this prediction, that is, showing a diminishing conductivity as the temperature increases, the theory of Endo[4] has been developed in relation to the various atomic constants as shown by equation (1) and Fig. 1.

Recent and extensive data, however, show some marked deviations from these theories, and there have been indications that these relations do not hold generally above 300°C.

In contrast with the theories of diminishing conductivity as temperature increases is the relation of Compton,[5] which shows a minimum conductivity as temperature is increased (Fig. 1). Compton's[5] agglomeration theory is given in equation (2).

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[1] F. Birch and H. Clark, "Thermal Conductivity of Rocks and Dependence on Temperature and Composition," *Amer. Jour. Sci.*, **238** [8] 529; [9] 613 (1940); *Ceram. Abs.*, **20** [5] 126 (1941).

[2] P. Debye, Vortrage über die kinetische Theorie der Materie und Elektrizität, p. 46; Göttinger Wolfskehlvortrage. B. G. Teubner, Leipzig and Berlin, 1941.

[3] A. Eucken, "Wärmeleitfähigkeit keramischer feuer fester Stoffe," *Forsch. Gebiete Ingenieurw.*, **3** (*B Forschungsheft*, No. 353), March–April, 1932; *Ceram. Abs.*, **11** [11] 576 (1932).

[4] Yositosi Endō, *Science Repts., Tôhoku Imp. Univ.*, **11**, 183 (1922).

[5] A. H. Compton, "Physical Study of Thermal Conductivity of Solids," *Phys. Rev.*, **7**, 341 (1916).

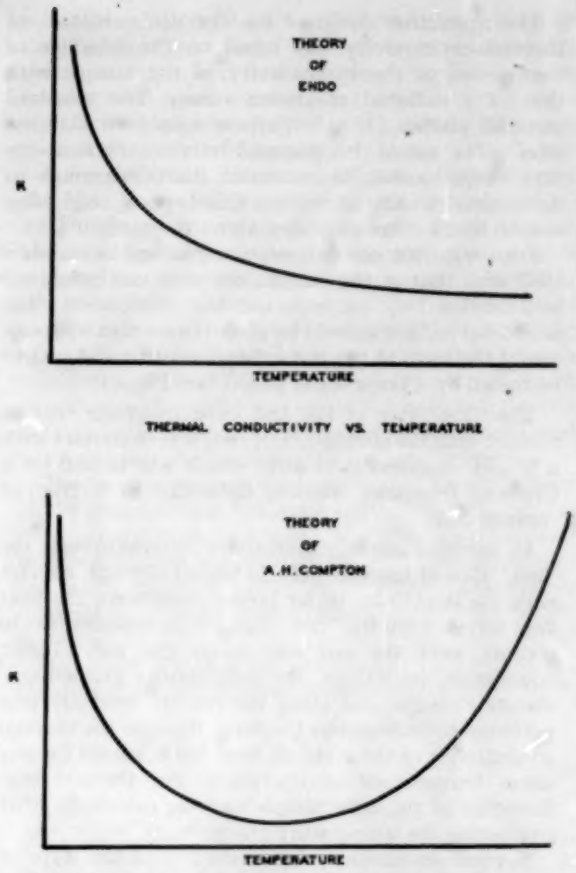

FIG. 1.—Endo and A. H. Compton theories of thermal conductivity.

Endo theory

$$K = 3\pi n k_0 \nu N a \left(\frac{h\nu}{k_0 T}\right)^2 e^{h\nu/k_0 T}/2(e^{h\nu/k_0 T} - 1)^{1/3} \quad (1)$$

n = numerical factor depending on character of space lattice.
k_0 = Boltzmann's gas constant.
ν = frequency of one of the lines in "rest-strahlen" of Rubens.
N = number of atoms per unit area perpendicular to direction of flow of heat in crystal.
a = "centered distance" between two neighboring atoms in direction of flow of heat.
h = Planck's constant.
T = absolute temp.

Compton theory

$$K = bn^2 dR\nu \cdot \frac{2 - cT^{1/3} \cdot e^{-B\nu/2T}}{c^2 T} \quad (2)$$

$b \neq 1$.
n^2 = number of atoms per unit area of plane normal to heat flow.
d = distance between "neighboring atoms."
ν = natural frequency of atoms.
c = conductivity at given temp.
B = universal constant.

The thermal conductivity of single crystals is affected by direction as well as by temperature, inasmuch as the laws governing the conduction of heat are similar to those governing the propagation of light. According to the summarization of the International Critical Tables,[6] the isothermal surfaces surrounding a single, constant, point source of heat in the interior of a crystal of any type are coaxial ellipsoids of constant axial ratios, provided the distance of the surface of the crystal from the source is great as compared with that of the isothermal surface. Crystals possessing cubic symmetry have the same thermal conductivity in all directions and therefore are thermally as well as optically isotropic. If a source of heat is conceived of at the center of a cubic crystal, the surfaces of equal temperature within the crystal are concentric spheres. Equation (3) is given for the general case, which expresses the relation between conductivities A, B, and C along the several principal axes of the isothermal ellipsoids as proportional to the squares of the lengths of the semiaxes.

$$\frac{x^2}{A} + \frac{y^2}{B} + \frac{z^2}{C} = 1 \quad (3)$$

x, y, and z = lengths of semiaxes

Thus, knowing the lengths of the axes of a crystal and assuming this relation to be sound, it should be possible to compute the ratios of the thermal conductivities along the axes of a crystal. It is not apparent how the theory of directional effects operates, however, when a crystal is studied at varying temperatures.

According to the predictions of theory, therefore, the effect of the crystals in a ceramic body on the thermal conductivity may be concluded to depend in turn on the temperature and directional effects in the crystals themselves.

In addition to the crystalline matter, a glassy phase is also found in many ceramic materials. The thermal conductivity of glasses varies with the temperature; the theory and experimental results indicate that (1) the relation is substantially linear at room temperature and higher and (2) the conductivity increases as the temperature is increased.

If the thermal conductivity characteristics of crystals and glasses are known (according to their proportions occurring in ceramic bodies), the heat conductivity characteristics of the body may be predicted. A third component of ceramic bodies may occur, namely, that of pores or voids, which are usually filled with air; these must also be considered. This investigation, however, is concerned only with crystals and some glasses.

II. Method and Apparatus

In testing for the thermal conductivity of single crystals of nonmetallics, a sample 1-cm. cube was used because of the difficulty in obtaining single crystals of any size. An additional advantage in cutting a single crystal into this shape was that it permitted conductivity tests along several axes with the same sample except for the monoclinic and triclinic crystals. When a cube is cut from a crystal of the tetragonal system

[6] International Critical Tables, Vol. 5 [Part I], p. 230 (1922).

(for example, so that each of two faces are normal to an axis), each of the other faces is also normal to an axis, and a desired crystallographic direction is obtained by turning the cube on to the proper face.

The cube samples were produced in the following manner: The single crystal was first examined for crystallographic faces, indicating the habit, and, if the faces were well developed, the position of the crystallographic axes could be determined and the cutting started. In cases where the single crystal showed no characteristic habit from faces, a face was cut on the crystal at random. A back-reflection Laue X-ray pattern was taken, and the orientation of the crystal was determined with the plot of Greninger. After the orientation was determined, the cube was cut roughly to size from the crystal with a "diamond saw" or a copper disk containing diamond dust in its edge. The piece was cemented with high-strength plaster of Paris into a steel ring, 2 in. in diameter and 1 cm. thick. The crystal was then ground with a silicon carbide abrasive on an iron lap wheel until the faces of the ground crystal were just even with the edges of the steel ring, which insured a distance of exactly 1 cm. between the two cut faces. After the faces were cut, the sample was removed and cemented in the ring again so that two more faces could be cut normal to the first two. A third repetition of this process produced the 1-cm. cube, whose size was checked with micrometer calipers. Cubes cut from transparent crystals were examined with the petrographic microscope to determine whether the crystallographic axis was normal to the face studied.

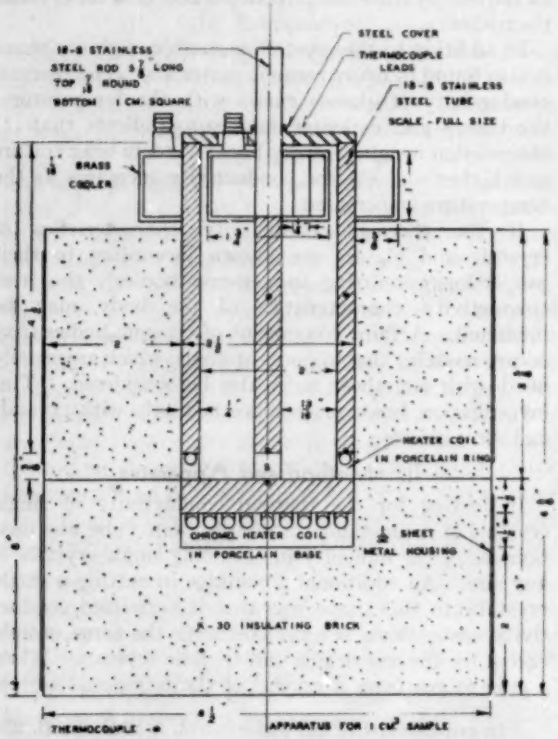

FIG. 2.—Section of assembled apparatus and sample.

The apparatus designed for the determination of thermal conductivity was based on the principle of comparison of the conductivity of the sample with that of a material of known value. The standard material chosen for this purpose was 18–8 stainless steel. The use of this material restricts the temperature range to definite maximum limits, inasmuch as detrimental scaling occurs on this type of steel after several hours at temperatures above 700° to 800°C.

For comparing the temperature gradient in stainless steel with that of the sample, the steel was machined into a rod of 1 sq. cm. cross section. The one end was milled flat so that it could be placed in contact with any one of the faces of the test cube; the other end was to be cooled by a brass water jacket (see Fig. 2).

The "hot" face of the test cube (opposite that in contact with the stainless steel rod) was in contact with a $2^1/_2$-in. stainless steel disk, which was heated by a Chromel resistance winding imbedded in a grooved ceramic disk.

In carrying out a conductivity determination, the "hot" face of the test cube is heated through contact with the steel disk; under proper conditions, the heat flow travels from the "hot" face to the opposite face in contact with the rod and along the rod. Under equilibrium conditions, the temperature gradients in the cube sample and along the rod are inversely proportional to their conductivities. Because the thermal conductivity of the stainless steel rod is known for any mean temperature of operation, the thermal conductivity of the cube sample may be calculated after comparing the temperature gradients.

Several precautions were necessary in this type of measurement. The prevention of sidewise heat flow from the sample or rod (to insure straight-line heat flow from the "hot" face of the sample through the rod) was maintained by situating the sample and rod inside a stainless steel "guard" tube, heated at one end by a resistance winding and cooled at the other so that a temperature gradient was produced in it almost identical to that in the sample and steel rod. Little lateral heat flow should exist when each portion of the rod is surrounded by an isothermal plane (Fig. 2); to insure this precaution, the air space between the rod and cylinder was filled in with crushed insulating firebrick.

Good thermal contact was also necessary at the sample-rod and sample-disk interfaces. A liquid film was therefore maintained in the interfaces by placing a piece of 0.001-in. pure tin foil, 1 sq. cm. in size, between the sample faces, rod, and disk faces. When the apparatus was heated, the foil melted at about 232°C., forming a fairly stable film of conductivity of the same magnitude as stainless steel. The temperature drop at the sample-steel interface may thus be considered negligible. Care was taken during the tests not to use the same tin film at higher temperatures for long periods of time because it does oxidize to some extent.

Inasmuch as the calculations in these determinations were based on the temperature measurements, careful attention was given to the methods for their deter-

mination. Temperature measurements were made on the "hot face" and "cold face" of the sample and at a point near the cold end of the rod. The thermocouples used were a combination of No. 30 Chromel and constantan wires, whose size allowed their use in a small space. Because the hot junctions of these couples could not be placed in actual contact with the "hot and cold" faces of the cube sample, they were situated in or on the stainless steel as close as possible to the cube faces; two couples were attached to the surface of the steel rod by spot welding the hot junctions on it, one very close to the milled end, which was in contact with the cube, and the other about 6 cm. away from the milled end. A hole was drilled in the stainless steel disk for a couple which extended to the center just under the surface in contact with the cube face. Extrapolation methods were used when necessary to determine the temperatures.

Thermocouples were also spot welded on the surface of the guard tube at the same horizontal levels as the rod thermocouple junctions. All thermocouple lead wires were taken into an ice bath (in a thermos bottle) for cold junction reference. The thermocouple readings were made with a semiprecision-type potentiometer.

Insulating firebrick insulation was clamped about the steel apparatus by sheet-iron bands (Fig. 3).

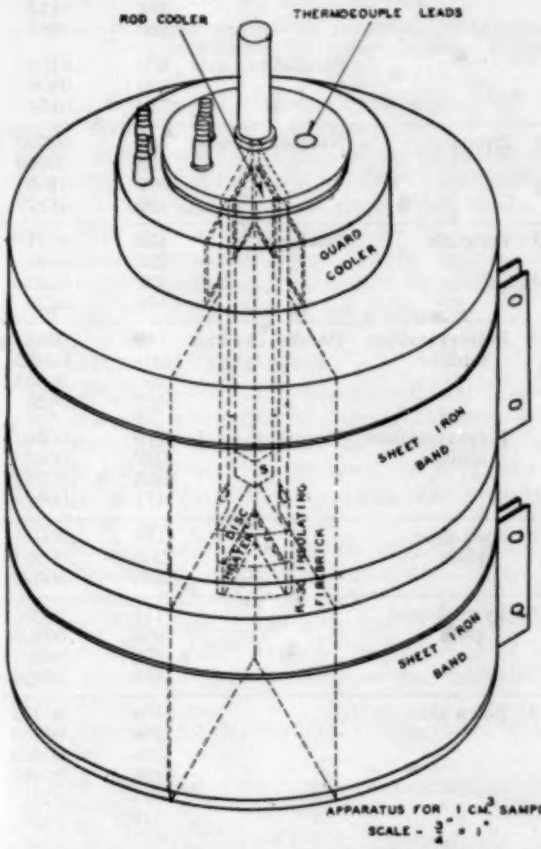

FIG. 3.—Apparatus for thermal conductivity determination.

The Chromel-constantan thermocouple was calibrated with the use of six standards for temperature.

The procedure for making a thermal conductivity determination (see Figs. 2 and 3) is described as follows:

The cut test cube is situated on the end of the stainless steel rod, placing a sheet (1 by 1 cm.) of 0.001-in. tinfoil in the sample-rod interface so that the cube face is exactly matched with the rod end face. A small film of collodion is then added at the interface edge to attach the cube. A square of tin foil is attached to the opposite cube face, and the apparatus is assembled, placing the cube, which is attached to the rod, inside the guard tube and in contact with the steel disk. The insulating material is inserted in this assemblage, filling the space between the guard cylinder and the rod. The test cube is held in place by the weight of the rod resting on it.

When the assemblage is completed, water circulation is started through the guard and rod coolers, and the current in the heaters is adjusted to bring the temperature of the apparatus at the steel disk to about 300°C. in two to three hours. This serves to melt the tin foil at the sample interfaces; at temperatures somewhat higher, it also oxidizes the collodion at the interface.

To obtain a reading, the currents of the disk and the guard-tube heaters are regulated until the temperature gradient in the guard tube is identical to that in the rod as indicated by like thermocouple generations on the rod and guard tube. The adjustments of water flow in the coolers may also be necessary to obtain this condition, and equilibrium is obtained when a "balanced" series of readings do not change over a two-hour period, a variation of ±0.05 mv. being allowed (approximately ±0.7°C.). The temperatures of the

TABLE I

DESCRIPTION OF TEST SAMPLES

Sample No.	Single crystals*	Color
1	Quartz (domestic), SiO_2	Colorless
2	Corundum (African), Al_2O_3	Red
3	Sapphire (synthetic), Al_2O_3	Colorless
4	Beryl (Brazil), $3BeO \cdot Al_2O_3 \cdot 6SiO_2$	Green
5	Tourmaline (Brazil), variable	"
6	Lithium fluoride (synthetic)	Colorless
7	Topaz (domestic), $Al(F,OH)_2AlSiO_4$	"
8	Zircon (Brazil), $ZrO_2 \cdot SiO_2$	Green
9	Periclase (synthetic), MgO	Colorless

Samples, not single crystals

10	Polycrystalline sample of electrocast mullite, in which the needles were well aligned			
11	Soda-lime glass composition			
		(%)		(%)
	SiO_2	69.73	K_2O	Trace
	Na_2O	20.96	R_2O_3	0.18
	CaO	9.05		
12	Pyrex-brand glass composition			
		(%)		(%)
	SiO_2	80.5	K_2O	0.4
	B_2O_3	12.9	Al_2O_3	2.2
	Na_2O	3.8		
13	Pure fused silica glass			

* All of the single crystals are (by nature) transparent except sample No. 2, which is translucent.

"hot" and "cold" faces of the test cube and the temperature gradient in the steel rod are taken at equilibrium for calculations.

After the determinations were made over the temperature range for one orientation of the cube, the apparatus was dismantled, and the cube was turned over so that a test might be made for another crystallographic direction.

Table I gives a description of the samples tested.

III. Results

The calculation of the thermal conductivity for a single crystal sample for any one temperature was based on a comparison of the temperature gradient in the cube sample with the gradient in the reference steel rod, inasmuch as they are inversely proportional as their conductivities. Because the thermal conductivity of the stainless steel rod is known[7] for any mean temperature, the conductivity of the crystal sample may be calculated by a comparison of its temperature gradient with that of the steel rod.

Figure 4 shows a composite graph of the crystal sample results, and individual curves are given in Figs. 5 to 10, inclusive.

IV. Discussion

(1) Apparatus

Because of the temperature limitations of the stainless-steel portions of the apparatus, the mean tempera-

[7] S. M. Shelton, "Thermal Conductivity of Some Iron and Steels Over the Temperature Range 100° to 500°C.," *Jour. Research Nat. Bur. Standards*, **17** [4] 441–50 (1934); R.P. 669.

TABLE II

RESULTS OF CALCULATIONS

	Sample No.	Orientation	Mean temp. (°C.)	Thermal conductivity*
1	Quartz	Parallel to *c* axis	100	0.0212
			145	.0174
			236	.0153
			308	.0137
			475	.0123
	"	Nomal to *c* axis	97	.00943
			100	.00950
			260	.00885
			383	.0104
			468	.0106
2	Corundum	Parallel to *c* axis	100	.0117
			302	.0160
			496	.0169
	"	Normal to *c* axis	99	.00950
			299	.0101
			477	.0143
			712	.0163
3	Sapphire	Normal to *c* axis	119	.00791
			238	.00925
			303	.0101
			490	.0144
4	Beryl	Parallel to *c* axis	120	.0104
			243	.0101
			340	.0118
			481	.0132
	"	Normal to *c* axis	126	.00996
			232	.0100
			304	.0104
			483	.0132
5	Tourmaline	Parallel to *c* axis	125	.00695
			267	.00765
			340	.00770
			450	.00838
	"	Normal to *c* axis	120	.00708
			219	.00826
			318	.00916
			456	.00996
6	Lithium fluoride	Isotropic	105	.00613
			249	.00932
			384	.0122
			499	.0138
7	Topaz	Parallel to *c* axis	94	.0123
			276	.0123
			484	.0168
	"	Parallel to *b* axis	99	.0112
			283	.0115
			520	.0168
	"	Parallel to *a* axis	100	.0105
			300	.0106
			512	.0151
8	Zircon	Normal to *c* axis	118	.00702
			252	.00950
			309	.0108
			499	.0127
9	Periclase	Isotropic	136	.0141
			236	.0181
			337	.0192
			499	.0226
10	Polycrystalline mullite	Parallel to *c* axis	119	.00888
			204	.00925
			290	.00945
			467	.0120
	Polycrystalline mullite	Normal to *c* axis	119	.00581
			227	.00632
			335	.00768
			471	.00913
11	Soda-lime glass		113	.00351
			205	.00391
			338	.00533
12	Pyrex-brand glass		115	.00365
			209	.00423
			352	.00597
			478	.00790
13	Silica glass		104	.00412
			214	.00458
			338	.00602
			488	.00835
			691	.0131
			819	.0185

* Thermal conductivity units = gm.-cal., sec.$^{-1}$, cm.$^{-1}$, °C.$^{-1}$. cm.

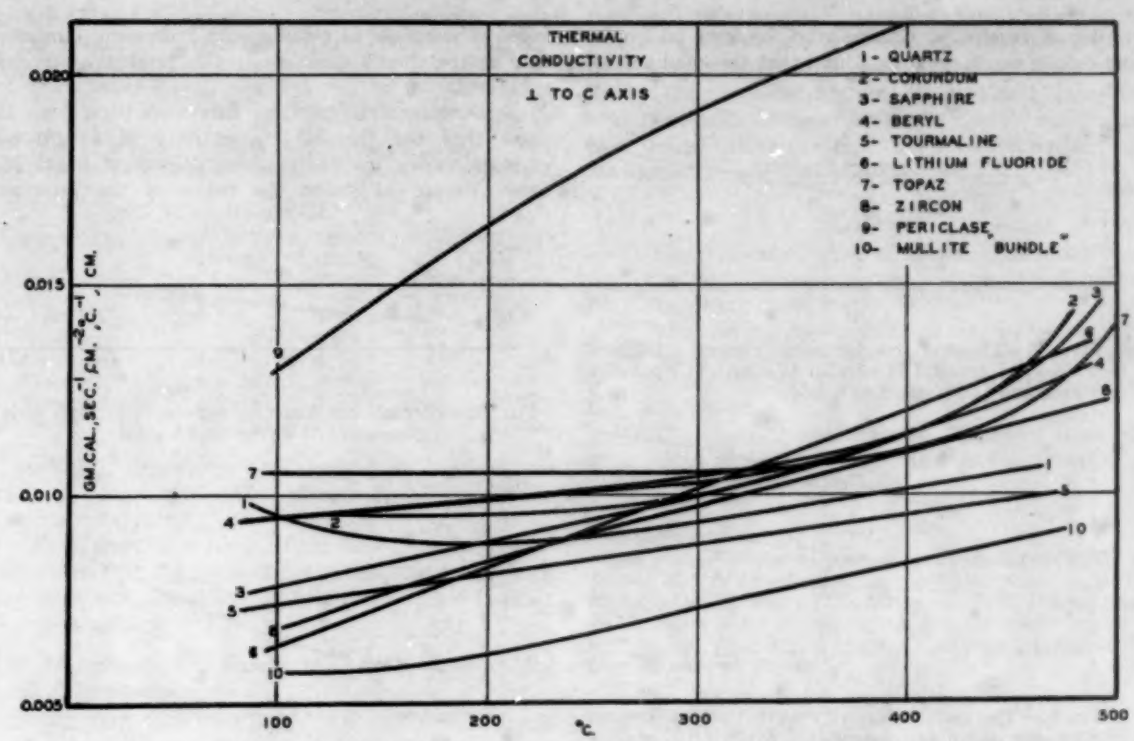

FIG. 4.—Thermal conductivity perpendicular to *c* axis; *curves*, (1) quartz, (2) corundum, (3) sapphire, (4) beryl, (5) tourmaline, (6) lithium fluoride, (7) topaz, (8) zircon, (9) periclase, (10) mullite "bundle."

tures of the thermal conductivity determinations did not exceed 600°C. except in a few cases.

The results given by the tests on quartz agreed well with those obtained by Birch and Clark[1] and Eucken,[2] and the values for the various glasses were similar to some offered by Eucken[2] and Kaye and Higgins.[3] Confirmation of the results was made for such samples as quartz, silica glass, and corundum by check determinations, which generally agreed within 5%.

(2) Theoretical Expectations

(*A*) *Single Crystals* (*a*) *Temperature Effect:* Curves (Figs. 4 to 10) show that the thermal conductivity, in general, does not continue to decrease with increasing temperature, as predicted by Eucken[2] and Endo[4] (Fig. 1) but that it increases with increasing temperature in the range tested.

In the case of tests on quartz and corundum, a minimum in the conductivity-temperature curves of each is noted, occurring near 100° to 200°C. This behavior is in agreement with the theory of Compton[5] (Fig. 1), which would explain the tendency of the single crystals tested to increase in conductivity above 200°C.

The presence of a minimum may be indicated by the

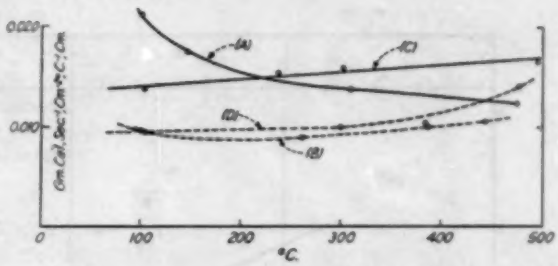

FIG. 5.—Thermal conductivity curves; quartz (*A*) parallel to *c* axis and (*B*) perpendicular to *c* axis; corundum, (*C*) parallel to *c* axis and (*D*) perpendicular to *c* axis.

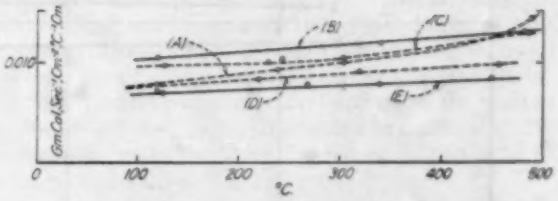

FIG. 6.—Thermal conductivity curves; sapphire (Al_2O_3), (*A*) perpendicular to *c* axis; beryl (A. D. Mackay) (*B*) parallel to *c* axis and (*C*) perpendicular to *c* axis; tourmaline, (*D*) parallel to *c* axis and (*E*) perpendicular to *c* axis.

[1] A. Eucken, "Über die Temperatureabhängigkeit der Wärmeleitfähigkeit fester Nichmetalle," *Ann. Physik* [Series 4], **34**, 35 (1911).

[2] G. W. C. Kaye and W. F. Higgins, "Thermal Conductivity of Metal Crystals: I, Bismuth," *Proc. Roy. Soc.*, **A113**, 335–51 (1926); *Ceram. Abs.*, **6** [6] 225 (1927).

results of Birch and Clark,[1] who, in tests on quartz and calcite single crystals, found that the conductivity failed to decrease as rapidly with increasing temperature as the theory demanded; this tendency was not explained.

(*b*) *Directional Effect:* The curves in Figs. 5 to 10 show that the thermal conductivity of anisotropic crystals varies markedly along the crystallographic axes. Figure 11 shows the ratios of the principal

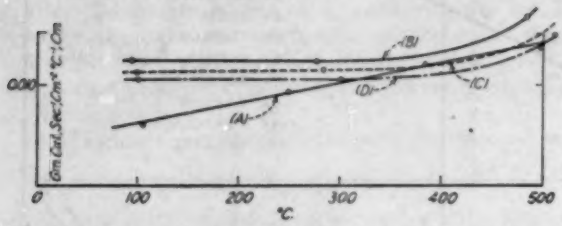

FIG. 7.—Thermal conductivity curves; lithium fluoride, (*A*); topaz, (*B*) parallel to *c* axis, (*C*) parallel to *b* axis, and (*D*) parallel to *a* axis.

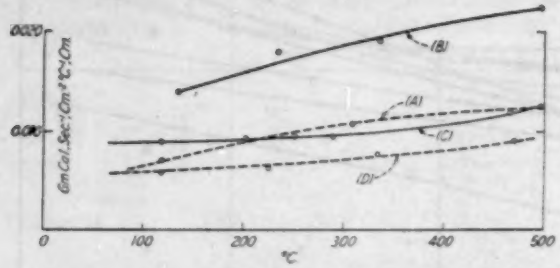

FIG. 8.—Thermal conductivity curves; zircon, perpendicular to *c* axis, (*A*); magnesium oxide, (*B*); mullite "bundle," curve (*C*) parallel to *c* axis and (*D*) perpendicular to *c* axis.

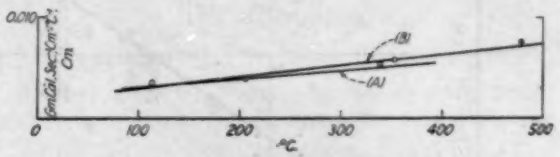

FIG. 9.—Thermal conductivity curves; (*A*) high soda glass and (*B*) Pyrex-brand glass.

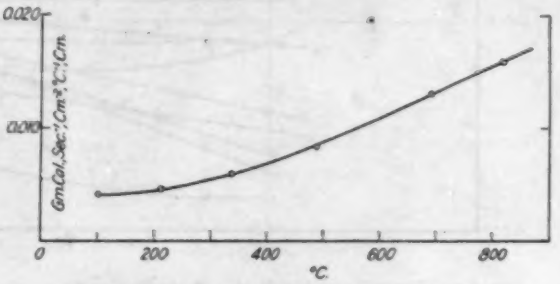

FIG. 10.—Thermal conductivity of fused silica.

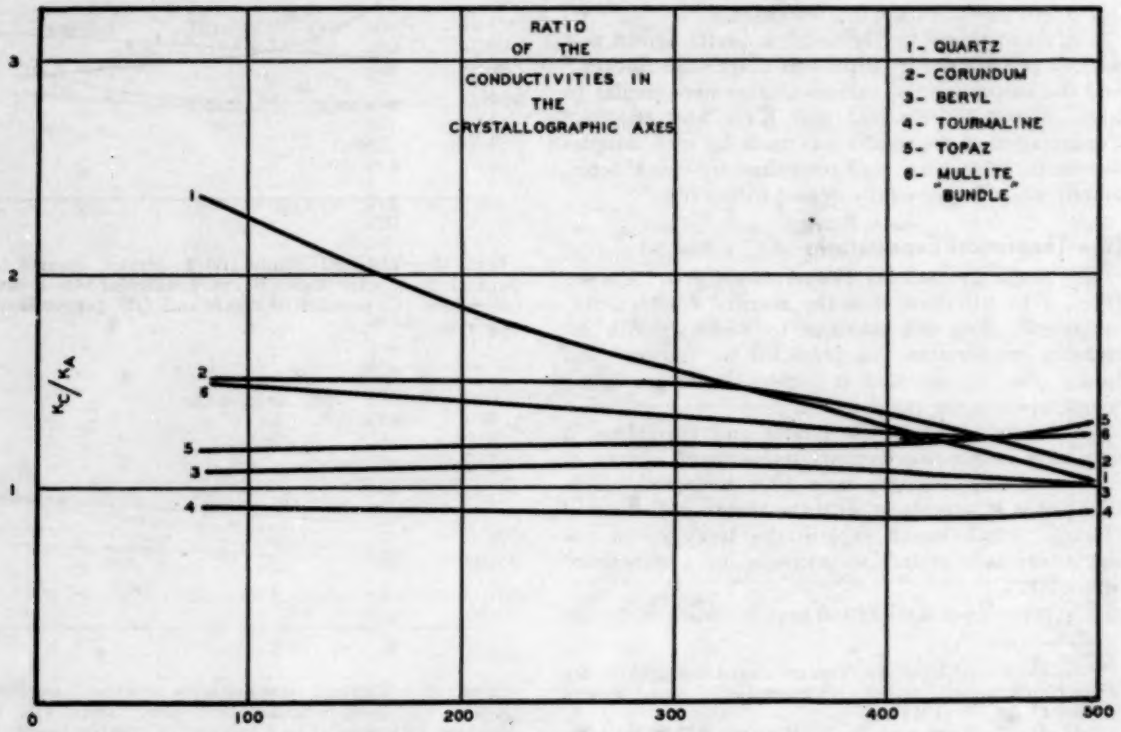

FIG. 11.—Ratio of conductivities in crystallographic axes: *curves*, (1) quartz, (2) corundum, (3) beryl, (4) tourmaline, (5) topaz, and (6) mullite "bundle."

conductivities in crystals. The calculated conductivity ratios, using equation (4), are compared in Table III with the experimental results.

$$\frac{a^2}{A}+\frac{b^2}{B}+\frac{c^2}{C}=1 \qquad (4)$$

A, B, C = conductivities along principal axes.
a, b, c = lengths of semiaxes.

TABLE III

DIRECTIONAL EFFECT ON THERMAL CONDUCTIVITY OF SINGLE CRYSTALS

Sample	a–c	C/A (calculated)	C/A (experimental) 100°C.	C/A (experimental) 400°C.
Quartz	1:1.100	2.79	2.22	1.30
Corundum	1:1.363	2.14	1.48	1.43
Beryl	1:0.499	3.76	1.10	1.09
Tourmaline	1:0.448	3.80	1.13	1.18
Topaz	1:1.788	0.80	1.17	1.23

This table shows the poor agreement between the thermal ellipsoid theory of directional effect and the experimental results.

(*B*) *Glasses:* The results from the tests on glasses agree well with theory, that is, the thermal conductivity increases with increasing temperature and is roughly linear in nature.

(3) Application of Results to Thermal Conductivity of Aggregates

Insufficient data have been obtained on the thermal conductivity of single crystals and glasses which occur commonly in ceramic bodies to allow for predictions. The temperature range investigated is also rather limited at the present time. It is hoped, however, that the results obtained on single crystals and glasses may aid in the explanation of the conductivity characteristics of common ceramic bodies.

V. Conclusions

(1) Single crystals give a minimum thermal conductivity with increasing temperature, which agrees with Compton's theory.[5]

(2) The thermal conductivity of single crystals may differ markedly in magnitude along the crystallographic axes, but this effect is reduced as the temperature is increased.

(3) The thermal conductivity of glasses increases with an increase in temperature and is roughly a linear function of temperature.

Acknowledgment

The author wishes to express his appreciation to G. B. Wilkes and F. H. Norton for their assistance; to S. F. Walton, Louis Navias, J. T. Littleton, Alexis Pincus, and W. R. Downs for supplying samples of single crystals and glasses; and to the Norton Company for supplying a periclase single crystal.

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ADSORPTION OF IONS BY LEACHED SURFACE FILMS ON GLASS*

BY HAROLD C. HAFNER AND FRANK L. JONES

ABSTRACT

The leaching of glass by acid or neutral solutions may be complicated by the selective adsorption of certain ions within the hydrated silica film formed on the glass surface. The rate of release of acid-soluble elements to the attacking solution is thus not necessarily in accordance with the amounts present in the body of the glass.

I. Introduction

The rate of release of soluble elements to a neutral or acid leaching solution is commonly not in accordance with the relative amounts of these materials in the glass. Collected data tend to prove that the difference between the rate of release of soluble elements to the solution is the result of preferential adsorption of some ions by the hydrated silica surface films. A promising method for studying this effect has been modeled after the general techniques used in chromatographic analysis. This method employs a long glass tube packed with a granular material of high adsorptive power. Specially prepared alumina is one of the most popular adsorbent materials. A solution containing several components, either organic or inorganic, is slowly flowed through the tube, whereupon the mixture will separate; the unadsorbed ions pass through the tube with the solvent, and the ions which the packing material adsorbs are concentrated in different zones. The strongly adsorbed ions will be concentrated near the top of the tube, and the less strongly adsorbed ions will be found in successive layers. Washing the tube with pure solvent will further separate the location of the various layers of different ions. If the ions are colorless, it is possible to make the layers visible by mixing a color-forming indicator with the solvent.

II. Test Methods

To study the effect of surface-film adsorption on the rate of release of acid-soluble elements in glass, the

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received June 8, 1942.

chromatographic technique was modified so that powdered glass was both the adsorbent and the source of the ions to be adsorbed. A tube, 60 by 1.5 cm., was filled with granules of dense flint glass powdered to pass a 50-mesh sieve. The glass contained approximately 50% of lead oxide, 7% of potassium oxide, and 43% of silica. Dilute nitric acid ($N/50$) was flowed through the packed tube. The solution was analyzed after passing through the column to determine the amount of material dissolved.

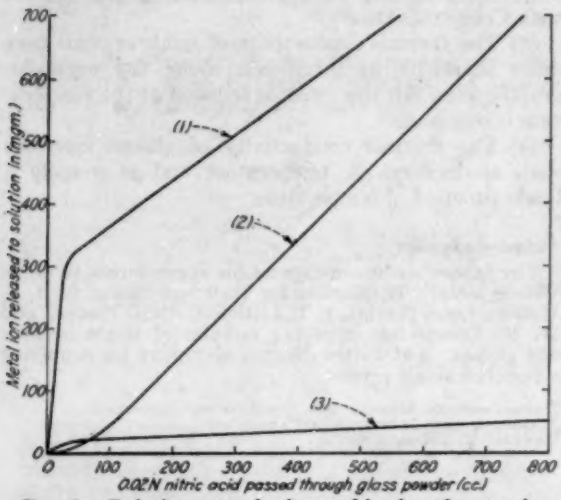

FIG. 1.—Relative rate of release of lead and potassium during passage of dilute nitric acid through powdered dense flint glass; curve (1), lead equivalent to amount of potassium released; (2) actual amount of lead released to solution; and (3) potassium released to solution.

III. Discussion of Results

As shown in Fig. 1, the potassium is released immediately in amounts large enough to show that a considerable depth of glass has given up its alkali. While the alkali is being released the rate of lead solution is small. As the release of potassium decreases, the rate of lead release increases. The hydrogen ions of the acid are removed almost quantitatively, supporting the idea that the reaction is one of exchange of hydrogen ions or oxonium ions for metal ions. These data indicate that a leached silica surface film has little power to adsorb potassium ions but is able to adsorb lead ions. The lead ions are partially adsorbed by a silica surface layer, whether they are being formed by ion exchange at the base of a surface layer or are contained in a solution in contact with the outer surface of a silica layer. Similar differences in adsorption are found with other glasses.

The difference in rate of solution is mainly caused by selective adsorption in the silica surface layer and not by the formation of two surface films of different properties as a result of the removal of both lead and potassium from the outer layer and removal of potassium only from a lower layer. Spectrophotometric curves of the light reflected from films of quarter-wave length and half-wave length thickness formed by a similar solution on a polished surface of this same glass have been compared. These films have the optical properties characteristic of a single film of uniform refractive index with a sharp lower boundary.

The chromatographic method for studying the leaching of glass is not so simple as those methods which determine only the rate of release of alkali. The results, however, are worth extra effort in that a more complete picture of the action of a solution on a glass is provided.

IV. Conclusions

The leaching of glass is not a simple solution process. It involves exchange reactions at the base of a permeable surface layer with selective adsorption characteristics for the various ions released from the glass.

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EFFECT OF CHEMICALLY FORMED SURFACE FILMS ON GLASS SOLUBILITY*

BY FRANK L. JONES AND HAROLD C. HAFNER

ABSTRACT

The leaching of acid-soluble oxides from a silicate glass forms a silica-rich surface film that is permeable to further acid attack. A quantitative study has been made of the effect of baking these surface films at various temperatures. The baking decreases the permeability of the films and thus makes the glass more resistant to attack by acid solutions.

I. Introduction

Under exceptional conditions it is possible to dissolve glass completely and uniformly in a solution. In many cases, however, glass solution involves only the more loosely held metal atoms with the basic glassforming oxide maintaining its network structure. Berger[1] investigated the rate of leaching of many different optical glass compositions with weak nitric acid solutions at a constant temperature and found that the depth of leaching can be related to the time of treatment by equation (1).

Berger found that the protective effect of the film pro-

*Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received June 8, 1942.

[1] Edwin Berger, "Principles Underlying Chemical Corrosion of Glass," *Jour. Soc. Glass Tech.*, **20** [80] 257–78 (1936); *Ceram. Abs.*, **18** [1] 13 (1938).

duced on a dense barium crown glass was so small that the constant b could be disregarded and the protective effect of the film for borosilicate and soda-lime-silica glasses was so marked that it was the important factor in the resistance of these glasses to acid leaching.

$$100t = ax + bx^2 \qquad (1)$$

t = time (hr.)
x = leached film thickness (μ)
a = constant depending on initial rate of action
b = constant depending on protective film effect.

The amount of light transmitted by a polished glass surface is increased when the glass is leached to form a transparent surface film of low refractive index. The optical industry has employed this type of antireflection film sporadically since 1892 on an empirical basis. One of the most serious troubles with this process was the fact that a lens often formed films of uneven character. It was seldom possible to treat a lens taken from stock and obtain a film of uniform thickness on the two surfaces. An assortment of previously invisible marks and fingerprints appeared in different colors in some cases. Experimental research on methods for controlling this process indicated that accidental formation of extremely thin silica films from contact with water or fingerprints takes place when the more soluble glasses are handled during manufacture. Operations that produce dehydration, such as the blocking of a finished surface in hot pitch for grinding and polishing of the second surface or heating when the lens is mounted for centering, will cause a densification of the silica film so that it is less penetrable to any subsequent leaching action. The leaching action presumably continues to follow Berger's equation but constant b is greatly increased. This type of protective silica film can also be purposely produced by leaching and baking a freshly polished glass surface.

II. Experimental Observations

Twenty-five different optical glass compositions have been studied to find out how to leach them on a controlled basis. Each was found to decrease in rate of leaching after densification of a thin, previously formed, surface film. Any glass to be used in contact with a solution that will dissolve some components of the glass but will not dissolve the network-forming oxide apparently can be improved in chemical durability by light leaching followed by baking. An interesting feature of this process is the decrease in permeability of the silica surface films far below the melting point of SiO_2. A quantitative study of the decrease in solution rate for different glasses indicates, however, that the densification of the surface film takes place faster at high temperatures. The baking temperature required to reduce the permeability of the surface film at a practical rate may be high or low depending on the composition of the glass. If the glass is high in silica, a high temperature baking is usually required. If the glass is high in soluble oxides and low in silica, the film will decrease in permeability even on drying at room temperature. Blodgett[2] noted a glass of this type while investigating low-reflectivity films. Water is given up by the film during the drying or baking, and the film decreases slightly in thickness. It seems probable that hydrogen ions or hydrated hydrogen ions replace the metal removed during leaching. Removal of water causes the observed volume shrinkage and the decrease in permeability.

III. Experimental Data

The following data illustrate the difference in baking required to change the solubility of a soda-lime-silica spectacle crown glass and a light barium crown optical glass. The solubility of the soda-lime-silica crown glass was determined by The American Ceramic Society powder solubility method No. 1. Because the light barium crown glass was not suitable for study by this method, the rate of leaching was measured by determining the time required to form a purple interference film (optical thickness of one fourth the wave length of green light). Table I shows the effect of leaching and baking on the rate of leaching by acid solutions.

TABLE I

EFFECT OF LEACHING AND BAKING ON RATE OF LEACHING BY ACID SOLUTIONS

Soda-Lime-Silica Crown

Filming-treatment			Heat-treatment		Acid leaching rate (%)
At 90°C.		Hr.	°C.	Hr.	
None			None		100
"			550	2	53
$N/50$ H_2SO_4		1	90	18	44
"	"	"	300	18	33
"	"	"	550	2	27
"	"	"	"	18	16
"	"	18	"	18	5
6 N HCl		3	90	18	29
" "	"	"	550	2	9
" "	"	"	"	2	<3

Light Barium Crown

Filming treatment		Heat-treatment (°C. for 1 hr.)	Acid leaching rate (%)
At 50°C.	Minutes		
None		None	100
"		100	53.4
$N/5$ HNO_3	5	Desiccator at 25°C.	2.4
" "	"	50	0.4
" "	"	100	<0.1

In the case of the soda-lime-silica glass, the change in solubility was produced on a freshly fractured surface; in the light barium crown glass, the surface was freshly polished with a slurry of rouge and water. The glass in each case was sufficiently homogeneous to be of optical quality. Commercial glass or enamel articles give erratic results after such treatment if the surfaces are grossly inhomogeneous or are fire polished.

IV. Conclusions

(1) The permeability of a leached surface layer on glass can be decreased by appropriate methods with consequent improvement in durability.

[2] K. B. Blodgett, "Use of Interference to Extinguish Reflection of Light from Glass," *Phys. Rev.*, 55, 391–404 (1939).

(2) The thickness of a leached film does not need to be great to produce a decrease in solution rate after densification.

(3) A thick film is more efficient protection than a thin film, unless the film is made so thick that it cracks and pulls away from the base glass when compacted.

(4) As the temperature of baking is increased, the protective effect of the surface film increases. This relationship no longer holds if the glass is heated to a point at which diffusion of material from the base glass into the surface layer becomes important.

(5) The baking temperature required to reduce the permeability of a leached film is generally higher for glasses containing larger proportions of network-forming oxides, such as silica and alumina, and lower for glasses containing more soluble oxides.

(6) Many of the older methods for increasing the durability of glass, such as contact with acid gases, salt vapors, or fused salts, probably involve differential removal of some metal ions from the glass surface and subsequent reduction of the permeability of a surface layer.

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AMBER GLASS AND THE ROLE OF CARBON*

By Henry Moore and S. R. Scholes†

Abstract

Melting experiments, employing batch materials free from sulfur but containing pure carbon in the form of sugar, demonstrate that carbon is not retained as a colorant. The value of carbon as a reducing agent in sulfur-bearing batches is confirmed, and the effect of iron is experimentally shown.

I. Introduction

The addition of carbonaceous materials to ordinary glass batches for the purpose of producing amber glass is an old procedure. In the absence of direct evidence to the contrary, the impression became established that carbon was the essential reagent responsible for the color. Even after sulfates and sulfides were introduced in connection with carbon, the name "carbon-sulfur ambers" became attached to these glasses.

As early as 1865, Pelouze[1] stated that reducing agents of different sorts, such as carbon and hydrogen, brought out in commercial glasses the same yellow coloration and that these were conditioned by alkali sulfides. In 1875, Benrath[2] attributed the color to the reduction of sulfates. Springer,[3] in 1919, held carbon responsible for the color. His view was supported in 1924 by Fedotieff and Lebedeff[4] and by Eckert and Zschacke. Fedotieff stated that it is possible to color glasses with sugar carbon and wood carbon when the glass batch is free from sulfate.[5]

Bontemps claimed that he prepared amber glasses free from sulfates, using only carbon. Long[6] says, "According to Bontemps, a beautiful yellow glass is obtainable with the following glass batch: sand 100, soda ash 45, calcium carbonate 35 to 40, and carbon from green poplar wood 4. He admits the presence of 2% of sodium sulfate (introduced by the carbonate) in the batch, which corresponds to 0.35% sulfur; he refuses, however, to believe that this quantity of sulfur is sufficient to produce the yellow color he obtains." Bork, in 1930, disputed the view that carbon was the colorant[7] and states, "No yellow coloration could be produced with raw materials free from iron and sulfur; on the contrary, the color came about immediately if only traces of iron and sulfur were present." Jebsen-Marwedel and Becker[8] also supported Bork. Weckerle,[9] in 1933, maintained that it was possible to get pure carbon coloration in soft glasses, but he also viewed iron sulfide as the colorant in normal technical glasses.

Fuwa[10] claimed that amber glasses were colored by colloidal carbon. He determined the carbon content in these glasses analytically and came to the conclusion that glasses were colored by colloidal carbon. His analytical procedure is as follows: "The glass was dissolved with hydrofluoric and sulfuric acids; the carbon was oxidized to carbon monoxide with chromic acid,

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941. Received August 29, 1942.

† This paper is based on part of the research conducted by the senior author for a Bachelor's thesis at the New York State College of Ceramics, Alfred, N. Y.

[1] Pelouze, *Ber. deut. chem. Ges.*, p. 802 (1865).

[2] H. E. Benrath, Die Glasfabrikation, p. 285. Vieweg und Sohn, Braunschweig, 1875.

[3] L. Springer, *Sprechsaal*, **52** [13] 88 (1919).

[4] P. P. Fedotieff and A. Lebedeff, "Absorptionspektra von gefärbten Gläsern," *Z. anorg. allgem. Chem.*, **134**, 87–101 (1924); abstracted in *Glastech. Ber.*, **3**, 19 (1925–1926) and **4**, 75 (1926–1927).

[5] For references to these writers, see C. Neumann and A. Dietzel, "Farbkörper in den sogenannten kohlegelben Gläsern" (Coloring Agent in So-Called Carbon Yellow Glasses: I, Coloring Glass with Colloidal Carbon), *Glastech. Ber.*, **16** [12] 389–91 (1938); *Ceram. Abs.*, **18** [4] 96 (1939).

[6] See Bernard Long, Propriétés Physics et Fusion du Verre, p. 138. Dunod, Paris, France, 1933; *Ceram. Abs.*, **12** [7] 260 (1933).

[7] A. Bork, "Färbung des Glases durch Kohle und Sulfide," *Glastech. Ber.*, **8**, 275–79 (1930); p. 276.

[8] H. Jebsen-Marwedel and A. Becker, "Über den Farbstich von Glas ohne Entfärbung," *Sprechsaal*, **63** [46] 874–78 (1930); abstracted in *Glastech Ber.*, **9**, 174 (1931).

[9] Hermann Weckerle, "Anfärbung von Gläsern durch Kupfer, Selen, und Schwefel," *Glastech. Ber.*, **11**, 273–85 (1933).

[10] K. Fuwa, "Glasses Colored by Carbonaceous Matter, I–III," *Jour. Soc. Chem. Ind. Japan*, **39** [9] 299–300B; [10] 373B (1936); reprinted in *Jour. Soc. Glass Tech.*, **20**, 333–37 (1936); *Ceram. Abs.*, **16** [3] 86 (1937).

then with air to carbon dioxide; the carbon dioxide was absorbed by potassium hydroxide; barium chloride was added to precipitate the carbonate; and the carbonate was filtered and titrated with hydrochloric acid."[11] The percentage of carbon was 0.0014 to 0.0197%. This work was reported in 1936 and 1937. Neumann and Dietzel[11] pointed out discrepancies in Fuwa's analytical procedure. They demonstrated that carbon was introduced into the analysis by sulfuric acid, hydrofluoric acid, and dust. They also obtained two samples of Fuwa's "carbon amber" glasses and analyzed them for carbon under dust-free conditions and with carbon-free acids. No carbon was found in either sample, but 0.98% iron oxide and 0.032% sulfur was found in each sample, and they concluded that sulfides and polysulfides were responsible for the amber color.[12]

Concerning the effect of iron oxide on the amber color, Hundeshagen[13] reported on a case as follows: "In consequence of local strong reduction by carbon, a black bottle glass came out instead of a green one. Here was the black coloring principle of iron sulfide. Upon analysis of the glass, not only sulfides but also polysulfides and carbonaceous substances were definitely found." Bork and Neumann and Dietzel, the most recent investigators of amber glass, agree that iron sulfide is a powerful colorant.

Relating to the question of the effect of furnace atmosphere and reducing and oxidizing agents, all authors agree that reducing conditions are essential for the development of the amber coloration; no data, however, were found on this subject.

Concerning the effect of alkali content on the color, Fedotieff states, "acid glasses are colored with difficulty; glasses rich in alkalis are colored easily."[6] Hodkin and Cousen[14] state, "The best type of glass for amber is soft, high-alkali glass; when the glass is more acid, carbon burns out."

II. Experimental Scope

A series of melting studies was undertaken in this laboratory to accumulate direct evidence on the nature of the amber coloration, particularly as to the coloring power of carbon alone and the necessity for its presence. It seemed desirable also to determine what modification in the color was produced by the presence of iron. Some attention was paid to the concentration of sulfur required and to the forms in which the sulfur could be introduced, that is, as element and as sulfate.

[11] C. Neumann and A. Dietzel cite K. Fuwa, see p. 390 of footnote 5.

[12] C. Neumann and A. Dietzel, "Farbkörper in den sogenannten kohlegelben Gläsern," (Coloring Agent in So-Called Carbon Yellow Glasses: II, Coloring of Heavy Metal-Free Glasses by Polysulfides), *Glastech. Ber.*, **17** [10] 286–90 (1939); *Ceram. Abs.*, **19** [3] 62 (1940).

[13] Franz Hundeshagen, "Zur Bestimmung des Eisen-Gehaltes in Blei-Mennige für Kristallglas; Kritik der in der Technik üblichen Analysenverfahren," *Glas-Ind.*, **37** [13] 194–95; [14] 203–204 (1930); detailed abstract in *Glastech. Ber.*, **7** [9] 396 (1929–1930); *Ceram. Abs.*, **9** [8] 625 (1930).

[14] F. W. Hodkin and A. Cousen, Textbook of Glass Technology, p. 130. D. Van Nostrand Co., Inc., New York, 1925; revised ed., 1937; reviewed in *Ceram. Abs.*, **4** [8] 235 (1925).

III. Method

A simple composition, selected for the parent batch, was SiO_2 75%, Na_2O 17%, and CaO 8%. Batches yielding approximately 700 gm. of glass were melted in crucibles under definitely reducing conditions except when it was planned to show the effect of an oxidizing atmosphere.

Sugar was used as the source of carbon in a pure form. In each group of glasses melted, at least one batch was included which was known to produce an amber glass under reducing conditions; the glasses were formed into small disks by pouring in an iron mold and rolling with a small roller.

Careful examination of the raw materials showed that the sand and soda ash were practically sulfur-free. The whiting, or precipitated calcium carbonate, used as the source of lime, contained a few tenths percentage of sulfate. A quantity of the whiting was converted into sulfur-free calcium carbonate by dissolving in hydrochloric acid, treating with barium chloride, and then with a little ammonium hydroxide, which threw down enough additional precipitate to furnish a flock; this rendered the barium sulfate easily removable by filtration. The resulting solution of calcium chloride was then treated with sodium carbonate and the precipitated calcium carbonate was filtered off, washed, and dried for use in the batches.

TABLE I

CARBON VERSUS SULFUR AND OTHER REDUCING AGENTS*

Melts	Whiting	$CaCO_3$	Salt cake	Sugar	Sulfur	Color
A_1, B_2, C_1	95		10	13		Strong amber
B_3	95			13	2	Light amber
B_4	95				2	" "
A_2, H_7, K_3	95			40		Pale amber
K_8	32	63		40		Faint yellow
A_3, H_3		95		40		None
A_5, B_1, K_7	95					"
B_5, C_3, K_3	95		10			"
C_4, K_4	95		10	(Al 2)		Strong amber
C_5	95		10	($SnCl_2 \cdot 2H_2O$ 17)		None

* Sand 500 and soda ash 195 or equivalent in all batches.

TABLE II

EFFECT OF IRON OXIDE*

Melts	Fe_2O_3 (%)	Color
D_1	None	Strong amber
D_2	0.4	Deep amber
D_3	0.8	Dark brown
D_4	1.2	Nearly black
D_5	1.6	Black
D_6	3.2	"

* Standard batch with salt cake 10, sugar 13, and Fe_2O_3 as given.

TABLE III

EFFECT OF SODIUM OXIDE*

Melts	Na_2O (%)	Color
F_1	17	Strong amber
F_2	22	Deep amber
F_3	27	Dark brown
F_4	12	Yellow
F_5	(K_2O 17)	Strong amber, matched F_1

* Whiting 95, sulfur 2, sugar 13, and Na_2O as given.

The salt cake, sulfur, and iron oxide used in some of the batches were ordinary commercial materials.

IV. Results

Tables I, II, and III give the results of the experimental meltings. Where the purified calcium carbonate was used, the material is designated as "$CaCO_3$;" "whiting" refers to the commercial material containing sulfate; and "none" refers to the absence of amber or yellow color, and these glasses were faintly green.

(*A*) *Effect of Oxidizing Atmosphere:* Parallel series of melts, one fired oxidizing and one reducing, showed that the amber color could be greatly diminished or prevented entirely by oxidation.

(*B*) *Effect of Varying Amounts of Sulfur:* Sulfur added to carbon as a reducing agent intensified the amber coloration but not proportionately. Carbon added as sugar in amounts less than that required to reduce the salt cake present produced no color.

(*C*) *Reproducibility:* Melts made in five separate runs, using salt cake 10 and sugar 13, produced glasses with scarcely any perceptible difference in color. With sulfur 2 and sugar 13, the colors varied in three runs from yellow to dark amber.

V. Conclusions

(1) Carbon, as such, is not a colorant of glass in the absence of sulfur or sulfate.

(2) Sulfur acts unreliably, either as a reducing agent or a sulfide former and with or without carbon, to produce amber glasses.

(3) Iron oxide intensifies the amber color to such an extent that it appears likely no amber would have been produced with the other reagents used in the complete absence of iron. The difficulty of getting iron-free materials and crucibles has prevented a demonstration of this point.*

Cadmium sulfide yellows are made, which are not amber in character but are related in color to the yellow of CdS. Lead glasses are also easily darkened or blackened by sulfur additions. It may be reasonable to infer that any of the heavy metals whose sulfides are dark would produce amber glasses in the presence of sufficient unoxidized sulfur.

(4) The increased intensity of amber color with increased alkali content merely confirms many published statements. This may be interpreted to indicate increased stability of iron sulfide as silica acidity decreases. Potash, in the single experiment made, showed no effect noticeably different from that of soda.

(5) The effect of oxidizing atmosphere follows from the known properties of sulfates.

(6) Sulfur, because it may readily boil away before forming sulfides, is not to be recommended for making reproducible amber glasses.

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* O. G. Burch, Owens-Illinois Glass Company Research Laboratory, states that he has obtained colorless glasses by making melts of iron-free batches containing sulfur-bearing materials under strong reduction.

SALT GLAZES FOR STRUCTURAL BUILDING UNITS*

By H. D. Foster

Abstract

The conditions necessary for the formation of a clear, transparent salt glaze on structural building units are described. Laboratory trials, which were made under these conditions or slight modifications of them, were studied by means of enlarged photographs of the surfaces and thin sections of the glazes. These pictures illustrate the process of formation of the glaze and show that glazes more than 0.001 in. thick are susceptible to crazing.

Salt glazes usually are formed from 0.003 to 0.004 in. thick in order to obtain a smooth brilliant glaze, but such glazes craze badly. Much better glazes may be obtained with only a sufficient number of saltings to give a glaze thickness of approximately 0.001 in., followed by a maturing or smoothing treatment in which the salting temperature is held for some time, or borax is used during the latter part of the salting and (or) the early part of the cooling period.

I. Introduction

Glazes are surface coatings on clay products which, during their formation at high temperatures, attain a glassy state and give an impervious coating to cover and protect the semiporous clay body. Salt glazes are the simplest and cheapest of all glazes. They are formed during the normal firing period of the clayware by the interaction of an alkali vapor on the acid silica constituent in the surface of the ware and the subsequent solution of the clay body to give a sodium-aluminum-silicate glaze of variable composition. The glazing process is carried out by the simple expedient of adding sodium chloride on the hot coals in the fireboxes or directly into the kiln so that it will volatilize and its constituents will

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pass over and around the ware to react therewith.

Although salt glazing is an old art, its technical aspects have been examined and understood only during recent years. The most general use of the process in America has been in the stoneware and sewer-pipe industries. It is also being used for light- or buff-colored structural building units, which are designed for exterior exposures where the glaze must retain its beauty and brilliance and give permanent protection. A considerable amount of technical work has been done on salt glazes for stoneware and sewer pipe.

Outstanding investigations have been carried out by Barringer, Neuman, and Fischer, and Schurecht. Their work, as well as that of others, has been critically examined, and a résumé has been given in a previous paper.[1]

II. Scope of Investigation

The findings of previous studies of salt glazing have been applied in the field of structural building units, and the results have been extended (1) by means of the formation and study of glasses of the approximate salt-glaze composition and (2) by the production and examination of many salt-glazing trials. The glasses having the most adaptable glaze compositions were subjected to solubility and thermal-expansion measurements. The glaze trials were examined for defects, and enlarged photographs of their surfaces and of interesting features in transverse thin sections of the glazes were studied.

Crazing has been considered to be the chief defect of the normal salt glaze. The results of this investigation have therefore been summarized to emphasize the cause of this defect and to suggest a method of correcting it.

III. Glaze Formation and Composition

A body suitable for salt glazing should have 3 or more mols of silica to each mol of alumina and should contain from 30 to 50% of finely divided and uniformly distributed silica for the best glaze adherence. The body should have a fine texture after it is fired so that a minimum amount of glaze will be required to obtain complete coverage and a smooth brilliant surface.

The ware should be well spaced in the kiln so that all of the surfaces will be freely exposed to the moving kiln gases. The firing should be continued nearly to the vitrification point or to that point where incipient fusion has set in on the surface of the ware. Small pools of molten glass will be formed into which matrix the larger silica and other body particles are embedded. At this stage of the firing, sodium chloride or common salt is added to the hot coals of each firebox where it vaporizes and is carried into the kiln.

The salt vapor reacts with the silica and water vapor to form the glaze and hydrochloric acid; the latter, which is more volatile, leaves the kiln quickly, but the sodium vapor should be held as long as possible. The kiln dampers should be partially closed during the glazing process, or some other precaution should be taken to maintain a continuous concentration of sodium vapor within the kiln. The clay for structural building units should have less than 1% of iron content, and the kiln atmosphere must be oxidizing throughout the firing and glazing operation. To assure a constant oxidizing atmosphere throughout the glazing period, a reasonable draft must be maintained and the salt must be added in small and frequent batches. The addition of salt to each firebox is considered as one salting, and from 15 to 18 saltings are necessary for a kiln containing light- or buff-colored building units. Sewer pipe, however, may be fired and glazed under reducing conditions with only five saltings.

IV. Salt-Glaze Glasses

(1) Formation of Glasses

Because the normal thickness of a glaze is only 0.001 to 0.003 in., it is impossible to collect glaze samples for a study of their physical properties. Glasses were therefore made with compositions ranging from 10 to 37.5% of Na_2O, 0.0 to 25% of Al_2O_3, and 50 to 70% of SiO_2. These glasses, formed from soda ash, kaolin, and flint were ground, mixed, and melted in small refractory crucibles. The small crucibles were placed in a sagger and heated in a laboratory kiln to 2200°F. so that the different batches would receive the same heat-treatment and give comparable glasses. The melted or partially melted batches were broken out of the crucibles, and the portions that were contaminated by the crucible were ground away.

The glass batches containing 15 to 22.5% of Na_2O, 15 to 20% of Al_2O_3, and 55 to 65% of SiO_2 could be considered as possible salt glazes at 2100° to 2150°F.; and the batch containing 20% of Na_2O, 20% of Al_2O_3, and 60% of SiO_2 was chosen as the most likely average for the salt-glaze composition.

When boron oxide was added to this average salt-glaze composition (a 20% B_2O_3 addition), a final composition of 16.6% of B_2O_3, 16.7% of Na_2O, 16.7% of Al_2O_3, and 50% of SiO_2 gave the best glaze of this type.

(2) Solubility

The solubility of a glaze increases with an increase in Na_2O content. Solubility was measured by boiling sized, ground (150- to 200-mesh) samples of the glasses for 1 hour in water and a 3% HCl solution. The glass containing 20% of Na_2O lost 0.10% and 0.85% and that containing 37.5% of Na_2O lost 9.81% and 14.0% in the water and acid solution, respectively.

(3) Thermal Expansion

Thermal expansion was determined by the interferometer method for a few of the glazes and for a typical body. Figure 1 shows curves for the 20% Na_2O glaze, for the same glaze with 20% of B_2O_3 added, and for the typical clay body. The coefficient of expansion over the range from room temperature to 350°C. (662°F.) of the relatively high Na_2O glaze was 11.61×10^{-6}; that of the clay body was 6.31×10^{-6}; and that of the B_2O_3 glaze was 9.06×10^{-6}.

V. Laboratory Glazing Trials

(1) Material

In order to study the technique of glazing clay struc-

[1] References to these writers are given by H. D. Foster, "Résumé of Technical Studies of Salt Gazing," *Bull. Amer. Ceram. Soc.*, **20** [7] 239–41 (1941).

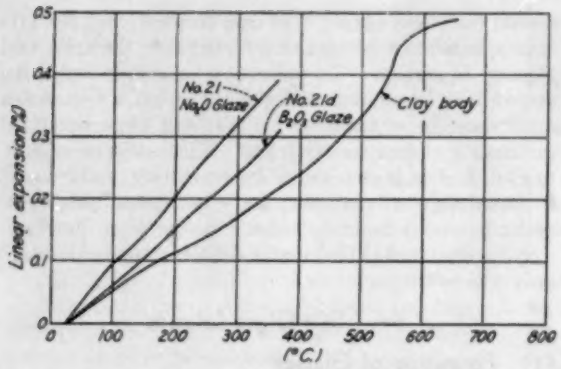

FIG. 1.—Thermal-expansion curves of typical glazes compared with specimens of clay body.

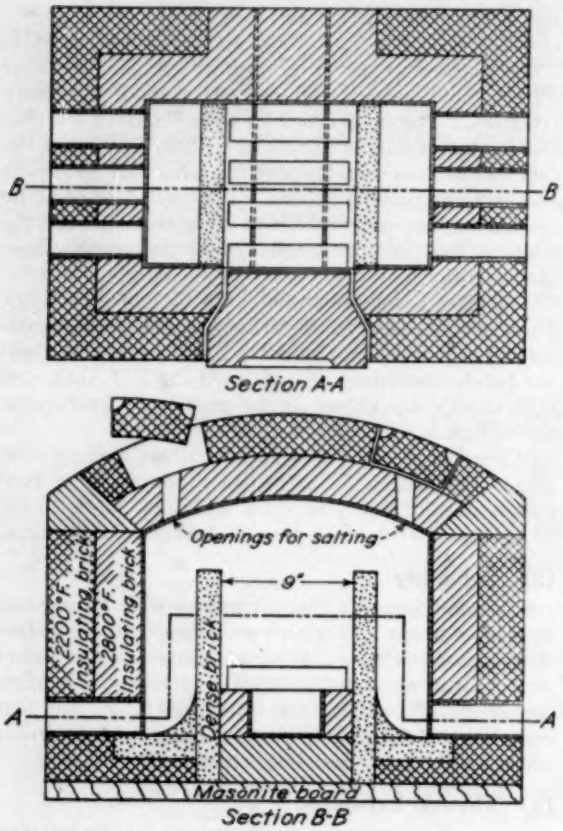

FIG. 2.—Laboratory salt-glazing kiln.

tural building units, unfired units were obtained from a plant producing only salt-glazed ware. The clay used at this plant was No. 5 or Lower Kittanning, which has an approximate ratio of 1.0 of alumina to 2.5 of silica, and a ferric oxide content of 2 to 3%. This alumina-silica ratio is changed to more favorable proportions for salt glazing by selecting and correctly proportioning the soft and sandy clay. The iron content is reduced by grinding so that many of the iron nodules may be removed.

A number of these unfired units were slowly prefired to cone 01 in a large laboratory kiln. These prefired units were used for quick firing and glazing in a small salt-glaze kiln.

(2) Salt-Glazing Kiln

A small kiln which had been built for a previous salt-glazing investigation was used for these trials. This kiln (Fig. 2) was built almost entirely of refractory insulating brick whose exposed surfaces were filled and sealed with a thick coat of air-setting, high-temperature cement. It was possible to fire the kiln to 2500°F. with three large Fischer laboratory gas burners on each side. The temperature was raised to 2100°F. in about six hours for all of the glazing trials. After being held at this temperature for about one-half hour, the glazing operation was carried out by inserting paper-wrapped, 5-gm. batches of the salting material into each side of the kiln at five-minute intervals.

(3) Trials with Progressively Increasing Amounts of Sodium Chloride

The amount of salt-glazing material required to give a definite amount of glaze is governed by the size of the kiln and by the method of draft control and introduction of the salt. The trials were fired with as oxidizing an atmosphere as possible to obtain a light- or buff-colored unit. The draft was reduced during the salting operation so that the kiln atmosphere was only slightly oxidizing. Preliminary trials under these conditions showed that 50 gm. of salting material, which was assumed to be the normal amount, would give the best results

A series of five trials was made, one half the normal amount of sodium chloride being used for the first member of the series. The amount of glazing material was doubled for each succeeding trial, and the changes in the surface of the glaze and its thickness with different amounts of salting were determined.

The surfaces of the trials were photographed with inclined illumination to show the crazing and other surface defects. Thin sections, cut transverse to the glaze surfaces, were also prepared so that the formation of the glaze and its structure might be studied. The average glaze thicknesses were measured from these pictures.

Figure 3 shows that the glaze formed with one half the normal amount of salt was not thick enough; that formed with a normal amount of salt was reasonably smooth and free from crazing; and when twice the normal amount of salt was used, some crazing occurred. Further trials, with larger amounts of salt, crazed badly.

TABLE I

GLAZE THICKNESS FROM INCREASING AMOUNTS OF SODIUM CHLORIDE

Amount of NaCl (gm.)	Glaze thickness (in.)
25	0.0008
50	.0019
100	.0024
200	.0035
400	.0038

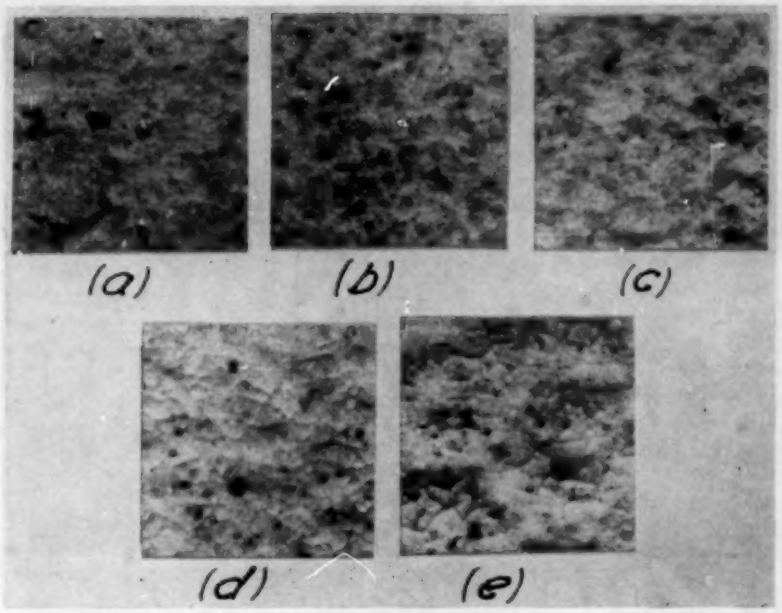

FIG. 3.—Enlarged photographs of salt-glazed surfaces: (*a*) with $^1/_2$ normal amount of salt; (*b*) normal amount of salt; (*c*) 2 times normal salt; (*d*) 4 times normal salt; (*e*) 8 times normal salt; × 5.

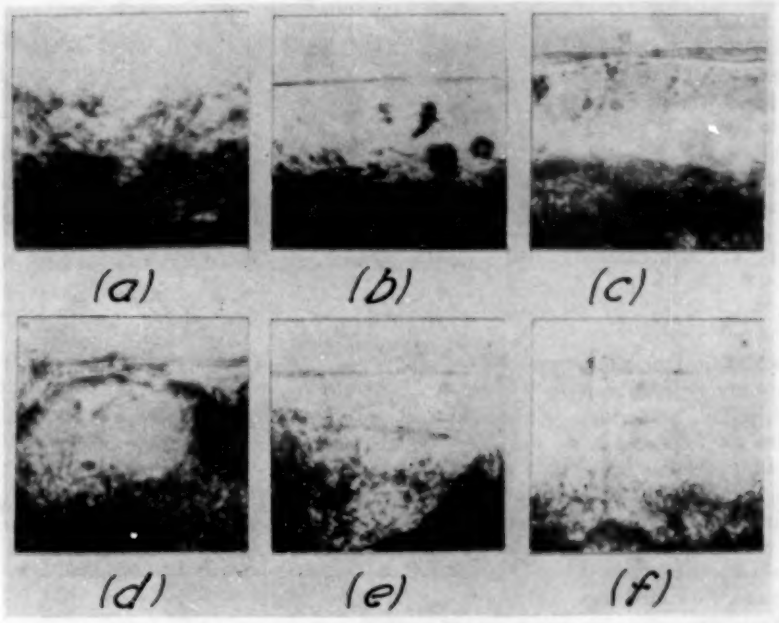

FIG. 4.—Thin sections of glazes showing increasing glaze thickness, × 250.

The thicknesses of the glazes of this series are given in Table I.

Figure 4 shows the increasing thickness of the salt glaze. Glaze (*a*), which contains only one half the normal amount of salt, is cloudy and penetrates the surface pores without dissolving the clay material; glaze (*b*) is clean and even, and glaze (*c*) is highly strained. Certain imperfections were revealed by the other pictures of this group; in one, a craze crack penetrates down through the glaze; in another, a large grain of quartz is barely covered; and in the third, the craze goes down to the silica particle, and a fracture occurs between the glaze and the silica grain.

(4) Oxidizing vs. Reducing Conditions

A direct comparison between the character of the glaze formed under strong oxidizing conditions and that formed under strong reducing conditions was obtained on separate glazed pieces taken from the webs of the same commercial unit. These two glazings were made under exactly the same conditions except for the kiln atmosphere during the firing and salting. In the one case, nearly 100% of excess air was used; in the other, the air was insufficient for complete combustion of the gaseous fuel.

The trial fired under the oxidizing conditions had a clear, thick transparent glaze which permitted the cream color of the clay body to show through the clear glaze; the glaze surface, however, was badly crazed (see Fig. 5). The photomicrograph shows a clear glaze about 0.0027 in. thick, with a sharp but irregular interface between the glaze and body. Numerous small quartz crystals were embedded in this lower layer of glaze, that is, the clay matrix originally surrounding the quartz had been dissolved. This interface, under a high-power microscope, appears not unlike a rocky irregular seashore.

The glaze produced under reducing conditions was entirely different in character (also shown in Fig. 5). It was almost 50% thicker (0.0039 in. thick) than the glaze formed under oxidizing conditions. Its general color was mahogany-brown, but close inspection showed it to consist of blood-red islands in a light-gray sea. The light-gray areas were filled with craze lines which were so fine that the glaze appeared to be crystalline. These craze lines, however, did not cross the blood-red

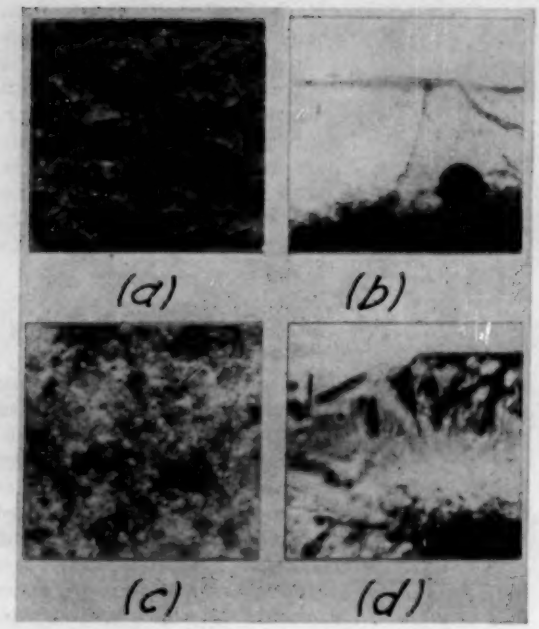

FIG. 5.—Glaze formed under oxidizing conditions: (*a*) surface, × 5; and (*b*) thin section, × 250; (*c*) and (*d*), glaze formed under reducing conditions.

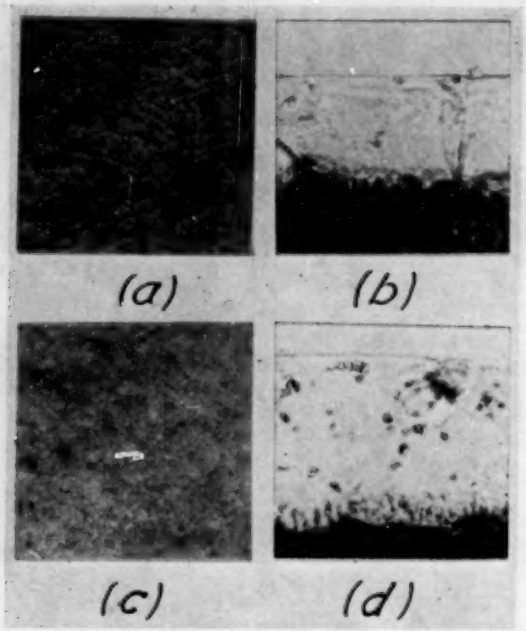

FIG. 6.—Commercial salt glaze: (*a*) surface, × 5; and (*b*) thin section, × 250; (*c*) and (*d*), applied or ceramic glaze.

islands, but stopped at their shores.

The reduced glaze showed many gas bubbles, some of which contained black material that was believed to have been carbon deposited in the pores near the surface of the piece during the firing or first part of the glazing. Some of these bubbles broke through the surface and left craters that were often only partially filled. The lower layers of the glaze were glass-clear, and the outer layers were colored with iron in solid solution or were filled with a network of hematite crystals.

(5) Trials with Borax

A few trials were made with salting mixtures for which 10, 20, and 33% of borax, respectively, had been substituted for equal amounts of sodium chloride. The glaze seemed to be thinner with each succeeding trial, although the same total amount of salt-glazing material was used for each of these trials. The brilliance and smoothness of the glaze increased, however, when reasonable amounts of borax were used with the salt. The results of these trials checked those obtained by Schurecht[2] in his study of salt glazing with mixtures of salt and borax or salt and boric acid.

VI. Examination of Commercial Glazes

Crazing is the most outstanding defect of salt glazes on structural building units, but this problem has not been mentioned in the older literature. Where glaze

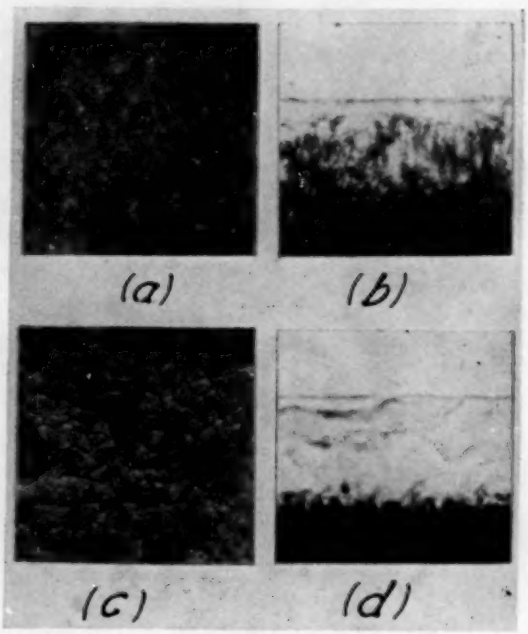

FIG. 7.—Two commercial salt glazes: (*a*) and (*c*) surfaces, × 5; (*b*) and (*d*) thin sections, × 250.

thicknesses were given, they were about 0.001 in. or less. Trial samples, 0.0018 in. thick, did not show much crazing. The usual thickness of the applied or ceramic glaze is approximately 0.004 in. (Fig. 6 (*d*)). Figure 6 (*a*) and (*b*), shows commercial salt glazes on

[2] H. G. Schurecht and K. T. Wood, "Use of Borax and Boric Acid Together with Salt in Salt Glazing," *N. Y. State Coll. of Ceramics, Ceram. Expt. Sta. Bull.*, No. 2, 1942; abstracted in *Brick Clay Rec.*, **100** [5] 36–38 (1942).

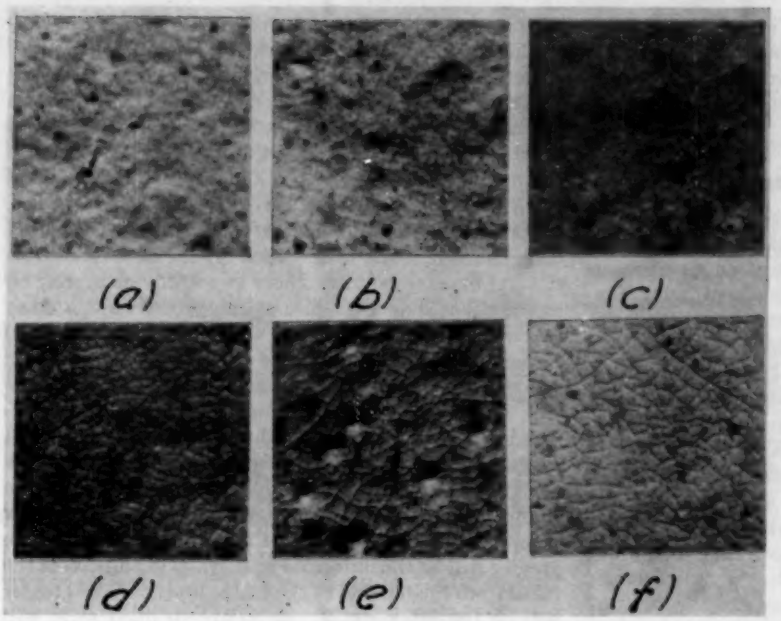

FIG. 8.—Surfaces of progressive draw trials from commercial kiln; trial samples taken after 3, 6, 8, 10, 14, and 18 saltings, × 5.

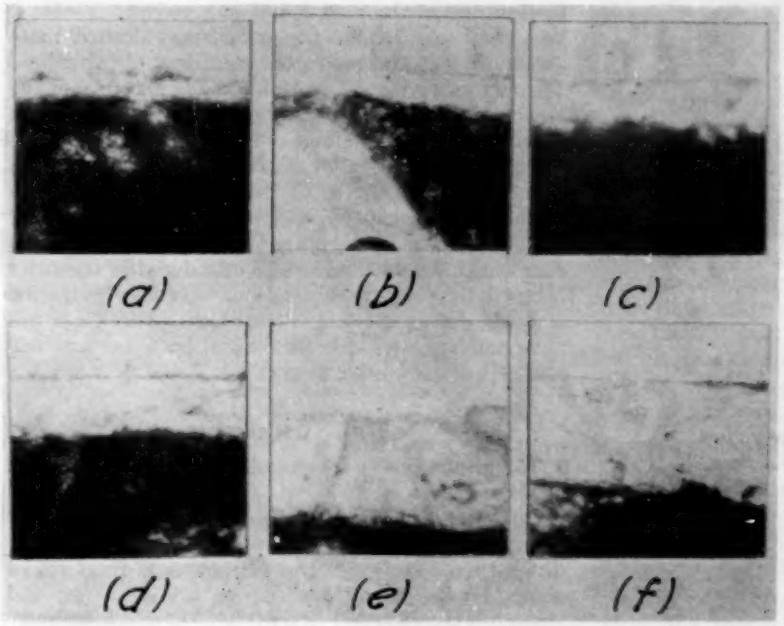

FIG. 9.—Thin sections of progressive trials from commercial kiln; trial samples taken after 3, 6, 8, 10, 14, and 18 saltings, × 250.

the same type of body. This glaze was about 0.0024 in. thick, and its surface showed craze marks which were very fine and close together. Two other commercial salt glazes are shown in Fig. 7. One of these had a bright glaze, Fig. 7 (*a*) and (*b*), which was free from crazing; the glaze surface was about 0.0008 in. thick with from 0.0008 to 0.0016 in. of additional thickness of body material imbedded in a glassy matrix. The other glaze, (*c*) and (*d*), was about 0.0027 in. thick and was smooth and brilliant but badly crazed.

(1) Draw Trials from a Commercial Kiln

A complete set of draw trials was taken after each round of salting of structural building units. These samples were made from No. 5 Ohio fire clay and were fired in a 32-ft. round, downdraft kiln. They were examined for glaze surface condition and glaze formation. The surfaces and sections of some of these trials are shown in Figs. 8 and 9.

The glaze was so thin after the third salting that the depressions in the surface of the body had not been filled. The surface of the glaze was much smoother after the sixth salting, but the low places in the surface had not been entirely filled or the high places leveled off. The glaze was not crazed after the sixth salting. When the glaze thickness averaged 0.0008 in. after the eighth salting, crazing began to show, but the lines were very fine. These trials were taken from the hot kiln and cooled rapidly after each salting. The glaze already formed under such conditions had no chance to mature or to smooth itself as it would by slow cooling.

The crazing began to show badly after the tenth salting, and small gas bubbles began to form in the glaze. These bubbles grew during the time required for the next few saltings and were breaking through the glaze so badly at the end of the twelfth salting that the surface of the glaze was rougher to the touch than the original unglazed trial. Nearly all of the gas had been evolved by the end of the fourteenth salting, but the craters left by the emerging bubbles had not all been filled. They were filled, however, by the end of the eighteenth salting, and the glaze was smooth and very thick but badly crazed.

The growth of the glaze may be clearly observed by a progressive examination of the photomicrographs of the thin sections. The clearest and most uniform glaze was obtained after the sixth to eighth salting. The glaze development was not complete with this number of saltings, but with additional saltings the glaze became

thicker and showed progressively increasing strain. If the temperature had been held for some time to permit the complete development of the glaze after the sixth or eighth salting, the best results probably would have been obtained.

VII. Discussion of Results

For salt-glazed structural building units, the trade demands a smooth and brilliant surface combined with permanence of appearance. The plant man can meet the first part of this requirement by continuing the glazing operation until the trial is sufficiently smooth, but this smooth glaze oftentimes does not retain its good appearance during service. The body texture may be coarse, and a very thick glaze will have to be built up before the surface is smooth. Such thick glazes craze even before the ware is taken from the kiln, but the crazing is very fine and is usually not apparent. The craze lines nevertheless extend down through the glaze to some imperfection in the body and then follow along that imperfection. In service, very fine dirt, such as soot, is carried by water into the craze cracks and then under the glaze to dull it and defeat its initial purpose.

Inasmuch as the chief defect in salt glazes is their tendency to craze, their improvement can be brought about only through an understanding of the causes of the crazing and a subsequent change of glazing technique that will eliminate or at least reduce the tendency to craze. This correction must be approached through an analysis of the formation of the glaze and its resulting, though variable, composition.

The main fundamental reaction in salt glazing is that between the hot acid silica in the surface of the ware and the basic alkali in the surrounding atmosphere. The chemical reaction usually accepted is a reciprocal reaction between sodium chloride, silica, and the ever-present water vapor. The reaction occurs in such a way that the hydrogen of the water binds itself with the chlorine of the salt to form hydrochloric acid, whereas the oxygen of the water combines with the sodium and the silica to form a sodium silicate. The sodium silicate thus formed dissolves sufficient alumina from the body to form an actual stable glass.

The amount of the glass formed is influenced by the concentration of the sodium chloride vapor in the surrounding atmosphere, by the temperature at which the salting is carried out, and by the size of the silica grains or attackable surface area. This conclusion implies that the body must have a low porosity so that there will not be many surface pores that must be filled with glaze. The silica must be readily available for the initial reaction. It has been stated that the body must have a ratio of 1 to 3 of alumina and silica with about 30 to 50% of free silica (finely divided). So much emphasis has been placed on the necessity of having a high content of silica that the manufacturers strive to get as sandy a clay as possible. In so doing, however, they obtain a body with a coarse texture which requires a very thick glaze to smooth out and cover the surface of the clay body.

The glaze grows both inward and outward, when it is once started by the initial fluxing of the silica in the clay surface. The growth outward results from the continued action of the glaze with the sodium chloride vapor to increase the sodium concentration gradually in the surface layers of the glaze. There is also an inward growth because the initial glaze in contact with the body continues to attack and dissolve the clay and silica particles in the surface layers of the clay body. The rate of the solution increases with temperature and decreases as the size of the silica grains increases. The silica grains, for example, those in a sandy clay, may be so large that they are attacked only slightly and are left as large grains imbedded in the glaze. It must also be recognized that as the glaze grows inward the sodium concentration decreases in these lower or inner layers. The thicker the glaze, therefore, the greater the variation in the sodium concentration between the outer and inner layers of the glaze. The sodium component of a salt glaze has from five to eight times as much influence in increasing the thermal expansion as any of the other components. The thicker the glaze, therefore, the greater will be the difference in thermal expansion of the glaze from the outside to the inside layers or the greater will be the inner strain. A highly strained glaze will craze.

When boron oxide is included in the glaze by borax or boric acid admixtures to the sodium chloride, the fusion temperature of the glaze is not only reduced so that a thin glaze can attain the smoothness desired more quickly, but it also lowers the coefficient of expansion. The factors developed by Hall[3] on the influence of the glass constituents on thermal expansion show that the effect of a given percentage of boron oxide will increase thermal expansion only one nineteenth as much as an equal percentage of Na_2O.

The greatest expansion of the salt glaze, whether thick or thin, is in the outer layers. The boron oxide component should therefore be introduced in the outer layers in as great a concentration as possible by the use of borax during the last few saltings. This glaze will have much greater smoothness and brilliance and will also be less susceptible to crazing.

VIII. Conclusions

The results of this investigation may be summarized as follows:

(1) The clay should (*a*) have a ratio of alumina to silica of not less than 1 to 3 and from 30 to 50% of finely divided free silica; (*b*) contain not more than 1% of iron; (*c*) be ground fine enough to give a fine and smooth-textured body; and (*d*) be fired to a sufficiently high temperature to give a dense body.

(2) The salt glaze is initially formed by the fluxing effect of the basic alkali on the acid silica with continued outward glaze formation by the reaction of the sodium chloride vapor on the initial glaze and with continued inward formation from the solution of the body by the initial glaze.

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[3] F. P. Hall, "Influence of Chemical Composition on Physical Properties of Glazes," *Jour. Amer. Ceram. Soc.*, 13 [3] 182–99 (1930).

(3) A salt glaze should not be more than 0.001 to 0.002 in. thick or crazing may occur.

(4) The composition of the salt glaze is variable, but it has a mean composition of about Na_2O 20, Al_2O_3 20, and SiO_2 60%. The Na_2O concentration in the glaze surface increases with the thicker glazes and decreases as the temperature of salting increases.

(5) A glaze may be obtained at a lower temperature by the partial substitution of borax for sodium chloride, and this glaze will be smoother and have less tendency to craze.

(6) The best salt glaze for structural-clay building units may be obtained by glazing under oxidizing conditions with only a sufficient number of saltings to produce a glaze approximately 0.001 in. thick, followed by a maturing or smoothing treatment consisting of holding the salting temperature for some time or by borax additions during the latter part of the salting and (or) early part of the cooling.

Acknowledgment

The author wishes to express his appreciation to all of his teachers, his adviser, and all associates in industry and at the Engineering Experiment Station who have assisted in many ways in connection with this investigation.

Engineering Experiment Station
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Columbus, Ohio

INFLUENCE OF SODIUM SILICATE COMPOSITION ON ITS BEHAVIOR WITH SODIUM CARBONATE AS A CASTING SLIP DEFLOCCULANT*

By Arthur E. Currier

Abstract

A study of six brands of silicate of soda used in a typical ceramic casting slip discloses the effect of the Na_2O to SiO_2 ratio on hydrometer readings, pH, viscosity, casting rate, water retention, drying shrinkage, dry strength, firing shrinkage, fired strength, and fired absorption. The effect of varying the amount of electrolyte both above and below that required for complete deflocculation is also reported.

I. Introduction

Ceramic casting slips are almost universally deflocculated by using a mixture of N-brand sodium silicate and sodium carbonate or sal soda. Each of the brands of sodium silicate is known to have definite and characteristic properties. This investigation was therefore undertaken to determine which of these brands is the best to use as a deflocculant for a body of this type and to find the relation of the properties of bodies to deflocculation above and below the optimum casting consistency. Simple physical measurements on the slip were taken on casting behavior, and the properties of the final cast product were determined.

The body composition was Klondike kaolin 22%, No. 12 Ky. ball clay 14%, No. 5 Tenn. ball clay 14%, flint 18%, and Buckingham feldspar 32%.

II. Method of Procedure

(1) Body Preparation

The ball clays were mixed in distilled water for 10 hours, and the kaolin was added and blunged for 2 hours. The nonplastic ingredients were added, and the complete body was blunged for 4 hours. This mixture was screened through a 120-mesh lawn and filter-pressed at a maximum pressure of 80 lb. per sq. in.

Five sets of filter-press cakes were thoroughly air dried in order to eliminate errors caused by aging; they were then crushed to pass an 8-mesh screen and stored until the tests were made. These samples were thoroughly mixed before and after crushing to insure a uniform batch.

(2) Preparation of Electrolytes

The deflocculants used were sodium silicates and c.p. anhydrous sodium carbonate. Table I shows the ratio of Na_2O to SiO_2 and other properties of the silicates. Each of these brands was used with sodium carbonate in a ratio of 60 to 40.

Because a gelation of the colloidal silica occurs as sodium carbonate is added to the sodium silicate, the electrolytes were added separately to insure accuracy.

The electrolytes were added in solution with concentrations of 1 cc. equal to 0.02 gm. of deflocculant. The solutions were prepared in sufficient quantity to last throughout the investigation.

(3) Deflocculation Tests

Each of the deflocculation curves consists of eight points, five of which represent compositions deficient in deflocculant, one containing the correct amount for complete deflocculation and two with an excess of electrolyte. Forty-eight sets of values for the six electrolytes were obtained. Each of these forty-eight bodies was made up separately.

The required amount of electrolyte was diluted to

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TABLE I

PROPERTIES OF SILICATES OF SODA*

Brand	$Na_2O:SiO_2$	Composition (%)			pH of concentrated solution	Sp. gr.	Viscosity (poises)	Approx. softening temp. of solids (°F.)
		Na_2O	SiO_2	H_2O				
S	1.0:3.90	6.3	24.6	69.1	10.8	1.300	2.6	2000
N	1.0:3.22	8.9	28.7	62.4	11.2	1.394	1.8	1575
K	1.0:2.90	11.0	31.9	57.1	11.5	1.480	9.6	1530
U	1.0:2.40	13.8	33.1	53.1	11.8	1.559	17.0	1525
C	1.0:2.00	18.0	36.0	46.0	12.2	1.692	700.0	1600
BW	1.0:1.60	19.5	31.2	49.3	12.7	1.676	70.0	1550

* From the Philadelphia Quartz Company.

552 cc. with distilled water and put in a large dish. The 1600-gm. batch was added to the liquid, thoroughly mixed, and the slip was transferred to a ball mill containing 25 small balls, which provided a mixing action and yet did no grinding.

After the mill was rotated for 6 hours, the specific gravity was checked by weighing 1000 cc. of the slip. Corrections were made, if necessary, and the mill was returned for 4 hours of additional mixing. Tests were made for specific gravity, viscosity, and pH values immediately after the removal of the mill. Precautions were taken at all times to prevent evaporation from the slip.

(4) Casting Tests

The slip was poured into a test mold for 30 minutes and drained for 10 minutes. After the excess was poured, the mold was shaken to obtain as clean drainage as possible.

The water present in the cast, expressed on dry weight basis, is termed the water retention. The dry weight of the cast is called rate of cast. After the tests were completed, the molds were dried in the air for 12 hours. This uniform drying eliminated to a large extent the variability caused by the molds.

(5) Bar Tests

The remainder of the slip was cast into eight bars, each 7 by 1 by $^3/_8$ in., and six bars, each 7 by 1 by $^1/_2$ in. These were dried for 12 hours at room temperature and for 12 hours at 220°F. Data were determined on drying shrinkage and on dry modulus of rupture. The structure of the bars was noted, and the dry modulus of rupture was determined by breaking the six thicker bars.

The remaining eight trials were fired in a plant tunnel kiln at cones 7 to 8. The bars were so placed in the kiln as to insure uniform heat-treatment throughout the entire set. Data on firing shrinkage, absorption, and fired modulus of rupture were then determined.

III. Description of Tests

(*A*) *Viscosity:* A Mariotte tube, used to measure the viscosity, was filled with 200 cc. of slip, the top was replaced, and the slip was allowed to stream into the graduate. The timing was made on the 100-cc. starting point at the 50-cc. mark and continued to the 150-cc. mark. This procedure was repeated until two values within 0.1 second were obtained.

(*B*) *Hydrogen-Ion Concentration:* The pH measurements were made with an L & N glass electrode pH meter which was balanced against a calomel electrode.

(*C*) *Specific Gravity:* The specific gravity was determined by weighing 1000 cc. of slip and also by the use of a hydrometer. The first value was kept constant at 1.830 throughout all tests, and the results of the hydrometer readings were noted. The hydrometer read from 60 to 70 Bé. or from 1.705 to 1.934.

IV. Discussion of Results

An important observation was made on the scum or skin formed on the top of the slip in the mold. This skin was visible on all samples, but the high soda silicates seemed to cause a tougher skin formation, and it was most tough at 0.10 to 0.12% of electrolyte additions. There was no trouble with thixotropic properties except for one body, which was so thick that it showed definite thixotropy.

Each of the properties that were measured and noted is discussed individually.

(1) Specific Gravity as Determined with the Hydrometer

These results were different from what was expected. There was no definite pattern although a trend could be seen. The specific gravity, which was determined by weighing, was constant at 1.830, whereas 1.837 was the lowest the hydrometer ever indicated, and it was more frequently found to be 1.847. The results therefore indicate that the hydrometer method of control is only relatively accurate and is not dependable.

(2) Hydrogen-Ion Concentration

The pH of the maximum deflocculation point, in general, decreased as the soda content of the silicate increased because less silicate is necessary for deflocculation when the high soda brands are used. The pH at which maximum deflocculation was obtained with each silicate was S 7.62, N 7.58, K 7.58, U 7.48, C 7.52, and BW 7.34.

(3) Viscosity

The viscosity curves show the expected decrease in viscosity with an increase of electrolyte. An interesting development was the marked decrease in viscosity with small additions of the high soda silicates, especially the

C brand. An addition of 0.02% of electrolyte to C-brand silicate gave the same viscosity as 0.06% of electrolyte to S brand. These high soda silicates, however, did not give minimum fluidity as did the low soda mixes.

The low soda silicate curves of Fig. 1 are much steeper, showing a greater range of viscosities. In the high soda varieties, the initial decrease was large with small changes from subsequent additions. This is shown by comparing the maximum and minimum relative viscosities, using the following different silicate brands: S 4.78, N 3.94, K 2.30, U 3.78, C 1.52, BW 2.46.

No strict correlation seems to exist between the soda content and the point of maximum deflocculation although the soda content at this point is usually higher when the high soda silicates are used.

These curves indicate that for viscosity the high soda silicates are superior when they are present in small amounts but that the higher the silica content the more fluid is the slip at the point of minimum fluidity. The low soda silicates are more effective in larger amounts than the high soda mixture.

The maximum deflocculation points for the curves in Fig. 1 fall within the range of 0.041 to 0.054% to Na_2O. It is apparent that the soda content is the most potent property of the deflocculant. This investigation does not substantiate the findings of other research relating to the effect of colloidal silica as an aid in the deflocculation process. These results, however, show that the soda content is more important than that of the silica except that the minimum fluidity is provided by a low soda mixture.

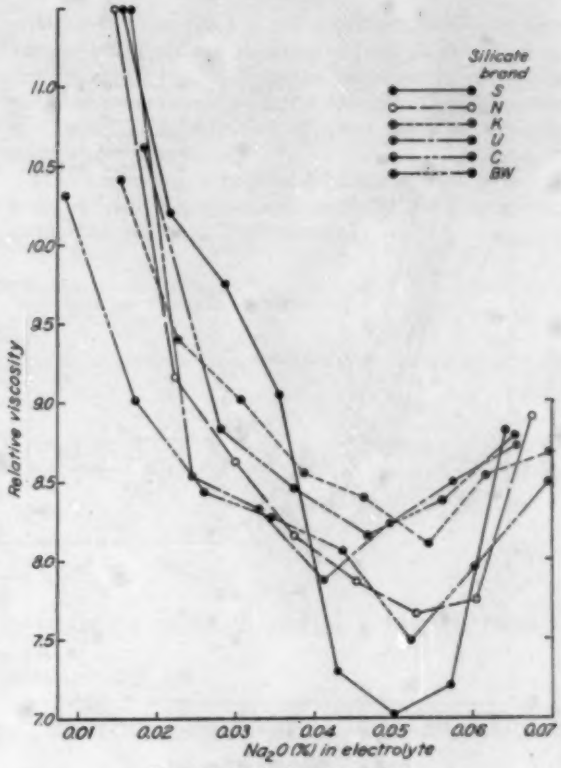

FIG. 1.—Relative viscosity.

(4) Casting Rate

The casting-rate tests were interesting because of the presence of an unexpected hump in the curve at the deflocculation point. Up to this point, the rate of cast decreased with an increase of electrolyte, increased at deflocculation, and then dropped back to normal with the next addition. This increase occurred when all six of the electrolytes were used (Fig. 2); with five of the six curves, the increase was at the exact point of maximum fluidity and the other was off only by 0.02%. This result cannot be explained because the molds were tested and were found to be practically the same and the casting time was kept constant. Additional tests could be conducted, although this effect is not important in commercial casting.

After the maximum deflocculation point was reached and the rate had dropped back to normal, the rate again began to increase as flocculation proceeded. A study of Fig. 2 reveals that at the same soda content, the high soda silicates generally increase the rate of cast. Another observation relating to Fig. 2 that cannot be explained is the division of the curves into two groups. Curves of silicates S, N, and K are bunched and those of U, C, and BW are bunched.

The casting-rate range (the difference between maximum and minimum weights), furthermore, decreased with the high soda silicates, an effect similar to that on the viscosity as previously noted. The range between maximum and minimum weights for each of the elec-

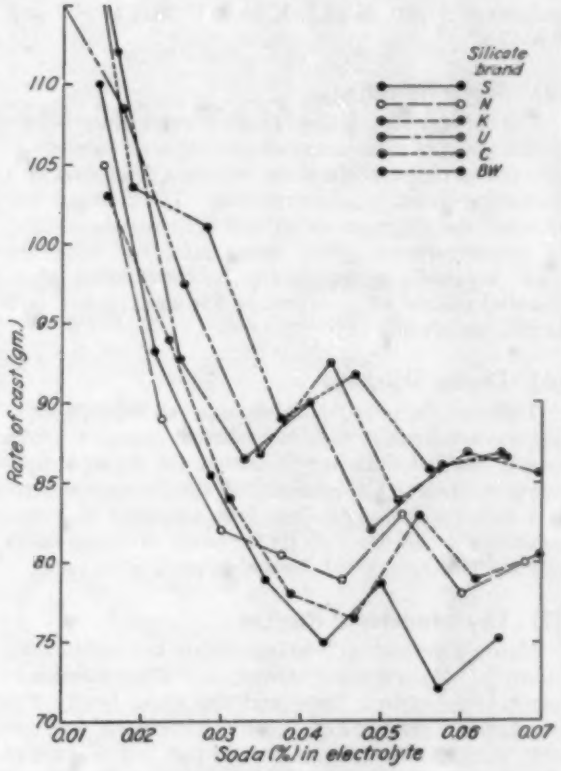

FIG. 2.—Rate of cast.

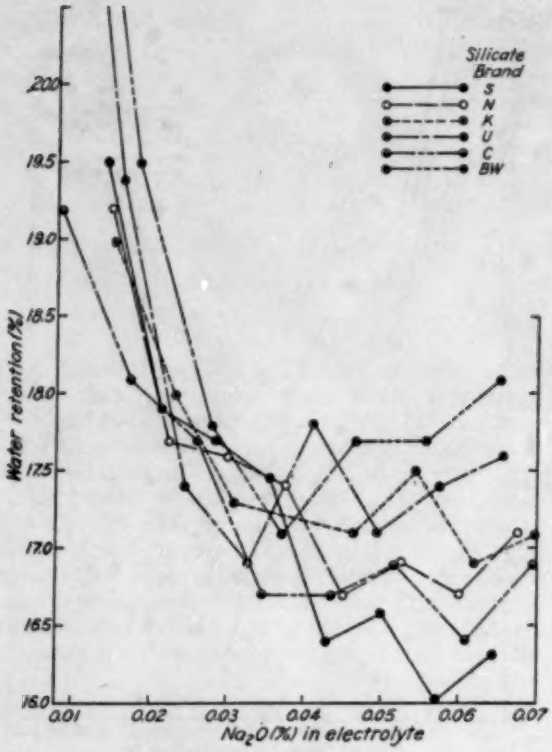

FIG. 3.—Water retention.

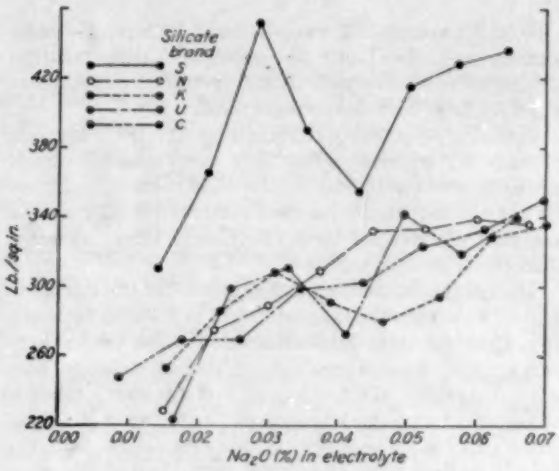

FIG. 4.—Dry modulus of rupture.

trolytes is S 48.0, N 34.2, K 34.9, U 30.0, C 24.7 and BW 17.8.

(5) Water Retention

The curves in Fig. 3 show that the same hump occurs at the point of maximum deflocculation as on casting-rate curves and that the water retention is lowered with increasing amounts of electrolyte. The S-brand silicate had the minimum value, and the low soda silicates in general showed lower water retention than the high, especially when greater amounts were used. C-brand silicate again is out of line as it is next to S brand, the lowest.

(6) Drying Shrinkage

Although the trend values obtained on drying shrinkage was apparent, it was not consistent enough to plot a graph. As deflocculation proceeded, the drying shrinkage decreased. The high soda silicates, in general, have less shrinkage than the low soda silicates. C brand again is the odd one with its shrinkage dropping below any of the others, which is another point in its favor.

(7) Dry Modulus of Rupture

Figure 4 shows that S-brand silicate has outstanding strength. No crust was formed, and other differences are visible between these and the other bars. The phenomenal strength of these compositions was the only outstanding characteristic in this test. Three of the silicates, S, K, and U, show an unexpected dip at 0.045% of Na_2O, which cannot be explained. The strength of the bars generally increases as the amount of electrolyte increases, and no marked difference is apparent between the low and high soda mixtures except in the case of S brand. BW-brand mixtures were not plotted because of an unintentional drying treatment of 350°F., which changed the results.

The ranges of values of modulus of rupture were close and showed no noticeable difference between different silicate mixtures.

(8) Firing Shrinkage

The firing shrinkage varied little with the different sodium silicates or by a comparison of deflocculated with flocculated bodies. The highest shrinkage recorded was 8.08% and the lowest was 6.80%. This gives a range of 1.20%, which could not possibly be considered large enough to permit definite conclusions. The only observation possible is that the shrinkage, in a general way, is less in the deflocculated than in the flocculated bodies.

(9) Fired Modulus of Rupture

The differences in the fired modulus of rupture results are so small that no definite conclusions are possible. The error resulting from firing and the experimental error probably are greater than the differences between the strength of the bars. The strength generally is higher as the percentage of deflocculant is increased, which could be expected because of the increased soda content and a consequent greater vitrification. There is no apparent difference, however, in the effect on fired strength of the low and high soda silicates.

(10) Water Absorption

The water-absorption results, as in firing shrinkage and fired modulus of rupture, are too similar to draw any definite conclusions. The absorption, however, decreases as deflocculation proceeds and then increases.

V. Conclusions

The use of N-brand silicate does not give properties outstanding enough to cause its use in the ceramic industry as a casting slip deflocculant. C-brand silicate imparts better properties than any other, namely, low viscosity with small additions of electrolyte, good casting rate, low water retention, good dry strength, and better than average fired properties. The difficulty in using this brand is its high viscosity but this may be overcome.

The high soda silicates in general have two important properties in that they are more effective in low concentration than the low soda silicates and they give curves which are not so steep and which should make control easier by reducing the variation in properties caused by variations in electrolyte addition. Because of the high concentration of these silicates, shipping costs would be reduced.

It is suggested, therefore, that these high soda silicates be tried in larger tests, especially the C brand because it shows unusual properties.

The Ohio State University
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President: M. D. Saindon, Chehalis Brick & Tile Co., Chehalis, Wash.
Secretary: W. P. Keith, Univ. of Washington, Seattle, Wash.

Pittsburgh
Chairman: E. E. Marbaker, Mellon Institute, Pittsburgh, Pa.
Secretary: H. E. Simpson, Mellon Institute, Pittsburgh, Pa.

Southern California
Chairman: J. E. Stevens, Emsco Refractories Co., South Gate, Calif.
Secretary: R. F. Evans, Gladding, McBean & Co., Los Angeles, Calif.

St. Louis
Chairman: H. H. Hanna, Pittsburgh Plate Glass Co., Crystal City, Mo.
Secretary: J. H. Ivery, Hydraulic Press Brick Co., St. Louis, Mo.